Non-Hamiltonian molecular dynamics: Generalizing Hamiltonian phase space principles to non-Hamiltonian systems

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The use of non-Hamiltonian dynamical systems to perform molecular dynamics simulation studies is becoming standard. However, the lack of a sound statistical mechanical foundation for non-Hamiltonian systems has caused numerous misconceptions about the phase space distribution functions generated by these systems to appear in the literature. Recently, a rigorous classical statistical mechanical theory of non-Hamiltonian systems has been derived, [M. E. Tuckerman, *et al.*, Europhys. Lett. **45**, 149 (1999)]. In this paper, the new theoretical formulation is employed to develop the non-Hamiltonian generalization of the usual Hamiltonian based statistical mechanical phase space principles. In particular, it is shown how the invariant phase space measure and the complete sets of conservation laws of the dynamical system can be combined with the generalized Liouville equation for non-Hamiltonian systems to produce a well defined expression for the phase space distribution function. The generalization provides a systematic, controlled procedure for designing non-Hamiltonian molecular dynamics algorithms which can be used to generate nonmicrocanonical ensembles, stationary nonequilibrium flows, and/or the dynamics of constrained systems. In light of this new general analysis, molecular dynamics algorithms for the canonical and isothermal–isobaric ensembles are examined, potential difficulties are illuminated, and the limitations of previous theoretical treatments are elucidated. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1378321]

I. INTRODUCTION

Non-Hamiltonian dynamical systems have a long history in mechanics (see, e.g., Ref. 1) and have recently been employed to study a wide variety of problems in the field of molecular dynamics (MD). In particular, non-Hamiltonian equations are used to describe driven systems, systems connected to reservoirs and/or mechanical pistons,[2–6] as well as constrained systems,[7,8] and systems away from equilibrium.[9–12] In equilibrium molecular dynamics calculations, non-Hamiltonian systems can be exploited to generate statistical ensembles such as the canonical (NVT), isothermal–isobaric (NPT) and isokinetic ensembles, which better represent the conditions under which experiments are performed than the standard microcanonical ensemble (NVE) generated by Hamiltonian dynamics.

In order to generate alternative statistical ensembles, "extended phase space" or "extended systems" are often employed.[13] Extended systems contain not only the N coordinate and momentum vectors needed to describe a classical N-particle system, but also a set of additional "control" variables designed to drive the fluctuations required by the ensemble of interest. Extended system equations of motion are usually closed with respect to the full set of dynamical variables, but not with respect to the classical subsystem (the variables describing the original classical N-particle system).

Various techniques have been proposed to extract the ensemble sampled by the physical system from the extended non-Hamiltonian dynamics. However, these prior approaches are not general. Hence, they are not reliable and can yield misleading or incorrect results. In order to properly understand and analyze non-Hamiltonian extended phase space methods, it is crucial to use the classical statistical mechanics of the underlying non-Hamiltonian systems[14] (based on the concepts of differential geometry as applied to dynamical systems,[15–17] in particular, pages 207–308 of Ref. 16) to develop a well defined procedure that leads to the phase space counterpart of the time averages generated in a dynamical study. It should be noted that the approach to non-Hamiltonian systems described in Ref. 14 differs from that presented in Refs. 10 and 7. These differences have been discussed in detail elsewhere.[12,14,18–20] This paper, in part, seeks to underscore the applicability of the results of Ref. 14, where modern techniques of differential geometry[15–17] are

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employed to derive a rigorous statistical mechanical theory of non-Hamiltonian systems, to problems in chemical physics, through clear, detailed, analytical examples and corresponding numerical demonstrations.

Consider, first, a Hamiltonian system, whose equations of motion do not depend explicitly on time, i.e., are autonomous. It is, well known, that the corresponding microcanonical partition function can be written as the integral over the positions and momenta times a product of delta functions expressing the constraints imposed upon the phase space by the conservation laws (the Hamiltonian, itself, and any others). This can be understood by noting that, in the canonical variables, Hamiltonian evolution preserves the phase space volume occupied by an ensemble of systems, i.e., the phase space is incompressible. It follows from the Liouville equation, which expresses the conservation of the phase space probability density, that the partition function of the ensemble is equal to the integral of a distribution function that can be expressed as a product of delta functions of the conserved quantities. Thus, all measurable points on a hypersurface in the phase space defined by the conservation laws obeyed by the system are visited with equal *a priori* probability.

Analogously, for a closed non-Hamiltonian dynamical system, it is clear that an equilibrium microcanonical ensemble in the full set of variables must exist. In order to properly define the microcanonical partition function over the full phase space, it is first necessary to determine the conservation laws of the associated dynamical equations. Once the conservation laws are known, linearly dependent variables and other trivial solutions are eliminated. The microcanonical distribution function can then be constructed from a product of δ functions that expresses the restrictions on the nontrivial phase space imposed by the conservation laws. Next, although non-Hamiltonian evolution does not preserve the phase space volume it, nevertheless, can be shown that an invariant phase space measure exists and is determined from a knowledge of the compressibility. This invariant measure is found to involve a nonunit metric. It, then, follows from the generalized Liouville equation for spaces with nontrivial metrics,[14] that the partition function can be expressed as the integral of the distribution function with respect to the invariant phase space measure.

The preceding paragraph defines a general, rigorous procedure for determining both the microcanonical distribution and partition function of any (equilibrium) non-Hamiltonian system assuming ergodicity. Note that it also applies to Hamiltonian systems written in a noncanonical form. In the case of extended non-Hamiltonian systems, the ''control'' variables can be integrated out of the full microcanonical partition function to generate both the distribution function and the ensemble sampled by the physical subsystem. It is important to note that *all* conservation laws obeyed by the system must be determined. Failure to account for all conservation laws is tantamount to assuming ergodicity on an incorrect hypersurface and can lead to incorrect conclusions about the phase space distribution generated by the dynamics.

This paper is organized as follows: In Sec. II, the statistical mechanical theory of non-Hamiltonian systems presented in Ref. 14 will be reviewed. In particular, the procedure for generating the invariant phase space measure will be discussed and the role of conservation laws satisfied by the equations of motion will be explored. We note, here, that the theoretical framework presented in Ref. 14 and in Sec. II differs from others in the field (see, e.g., Refs. 10, 21, and 22). This work serves to underscore the utility and power of the approach presented in Ref. 14, where modern techniques of differential geometry[15–17] are applied to non-Hamiltonian dynamical systems, to approach problems in chemical physics. In Sec. III, specific criticisms of existing approaches are given with reference to specific examples to follow in Secs. IV–VI. In Sec. IV, non-Hamiltonian systems used to generate the isokinetic and canonical (NVT) ensembles will be examined. In particular, it will be shown how and under what circumstances these algorithms fail to generate the canonical distribution. In Sec. V, the same analysis will be applied to equations of motion designed to treat the isothermal–isobaric (NPT) ensemble. In Sec. VI, non-Hamiltonian equations of motion used to treat systems subject to holonomic constraints will be analyzed. It will be shown that the non-Hamiltonian formalism leads to a phase space metric that precisely and correctly weights the phase space according to the condition that the constraint and its first time derivative are fulfilled as discussed in Refs. 23–28. Conclusions will be given in Sec. VII.

II. GENERAL THEORY

A. Physical basis and philosophy

We seek to generalize the usual Hamiltonian based statistical mechanical phase space principles to non-Hamiltonian systems. The standard Hamiltonian picture is defined by a set of evolution equations of the form

$$\dot{x} = G(x), \tag{2.1}$$

where x denotes a set of canonical variables $\{q,p\}$ with the equations of motion derived from a Hamiltonian $H(q,p) = H(x)$, i.e., $G(q,p) = \{\partial H/\partial p, -\partial H/\partial q\}$. Liouville's theorem guarantees that there is an invariant phase space measure dx. This means that a collection of initial conditions to Eqs. (2.1), $\{x_0\}$, occupying a phase space volume dx_0 will occupy the same phase space volume at time t under the evolution of Eqs. (2.1):

$$dx_0 = dx_t. \tag{2.2}$$

Thus, given an ensemble of systems described by the Hamiltonian $H(x)$, the phase space distribution function $f(x,t)$ of the ensemble, which satisfies the Liouville equation,

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \dot{x} \cdot \nabla f = 0, \tag{2.3}$$

is conserved. Suppose that Eq. (2.1) possesses n_c conservation laws of the form $\Lambda_k(x) = \lambda_k$, $k=1,...,n_c$. These conservation laws include the Hamiltonian itself, and any other conservation laws the system might possess. Then, since the equations of motion are assumed to contain no explicit time dependence, a meaningful (unnormalized) equilibrium solution to Eq. (2.3) exists and takes the form

$$f(x) = \prod_{k=1}^{n_c} \delta(\Lambda_k(x) - \lambda_k). \tag{2.4}$$

That is, the system will be restricted in phase space to the intersection of the hypersurfaces defined by the conservation laws. Therefore, the number of microscopic states Ω available to the system, which determines the partition function of the system, will be given by

$$\Omega = \int dx_0 f(x_0) = \int dx_t f(x_t) = \int dx f(x). \tag{2.5}$$

Thus, if the dynamical system defined by Eqs. (2.1) is ergodic, then the phase space average of any observable $A(x)$ defined by

$$\langle A \rangle = \frac{1}{\Omega} \int dx A(x) f(x) \tag{2.6}$$

can be equated to the time average

$$\bar{A} = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt A(x_t) \tag{2.7}$$

over a trajectory generated by Eq. (2.1). In the next subsection, a novel generalization of these principles to non-Hamiltonian systems[14] is described.

B. The generalized invariant measure

Consider a general dynamical system of the form

$$\dot{x} = \xi(x,t), \tag{2.8}$$

where x is an n-dimensional vector, $x = (x_t^1, \dots, x_t^n)$, and $\xi(x,t)$ is an n-dimensional vector function of x and t. Equation (2.8) is solved subject to a set of initial conditions $x_0 = (x_0^1, \dots, x_0^n)$. The solution leads to a set of n vector functions that depend on time and on the initial phase space coordinates

$$x_t^i = x_t^i(t; x_0^1, \dots, x_0^n). \tag{2.9}$$

Equation (2.9) can be viewed as a coordinate transformation from the initial coordinates at time, t_0 to the coordinates at time t. Thus, using Eqs. (2.8) and (2.9), it is possible to determine how the initial phase space volume element dx_0 transforms under Eq. (2.9). This is determined by the Jacobian of the coordinate transformation, Eq. (2.9)

$$dx_t = J(x_t; x_0) dx_0, \tag{2.10}$$

where

$$J(x_t; x_0) = \frac{\partial(x_t^1 \cdots x_t^n)}{\partial(x_0^1 \cdots x_0^n)}. \tag{2.11}$$

Since $J(x_t; x_0)$ is the determinant of a matrix, M, where $M_{ij} = \partial x_t^i / \partial x_0^j$, it can be shown (see, e.g. Refs. 14, 29, and 30) that $J(x_t; x_0)$ satisfies an equation of the form[14,31]

$$\frac{d}{dt} J(x_t; x_0) = J(x_t; x_0) \nabla_{x_t} \cdot \dot{x}_t = J(x_t; x_0) \kappa(x_t, t) \tag{2.12}$$

subject to the obvious initial condition $J(0) \equiv J(x_0; x_0) = 1$. A derivation of Eq. (2.12) is given in Appendix A. The quantity $\kappa(x,t) = \nabla_x \cdot \dot{x} = \nabla_x \cdot \xi(x,t)$ is known as the *compressibil-*

ity of the dynamical system with ∇_x the n-dimensional gradient operator in the phase space coordinates.

For a Hamiltonian system, the compressibility vanishes, so that $J(x_t; x_0) = 1$ for all time, which leads to the familiar conservation of the "Euclidean" phase space volume element dx,[32] according to Eq. (2.10), which indicates that phase space is flat.[33] For a non-Hamiltonian system, however, the compressibility need not vanish. In this case, it follows that the usual phase space measure dx is no longer an invariant measure under the dynamical evolution. In fact, the general solution to Eq. (2.12) is

$$J(x_t; x_0) = \exp\left(\int_0^t \kappa(x_s, s) ds\right). \tag{2.13}$$

Since $\kappa = d \ln J / dt$, Eq. (2.13) can be written in the form[14]

$$J(x_t; x_0) = e^{w(x_t, t) - w(x_0, 0)}, \tag{2.14}$$

where $w(x,t)$ is the indefinite time integral of $\kappa(x,t)$. Substituting Eq. (2.14) into Eq. (2.10) and rearranging leads to[34]

$$e^{-w(x_t, t)} dx_t = e^{-w(x_0, 0)} dx_0. \tag{2.15}$$

Equation (2.15) shows that the measure $\exp[-w(x_t, t)] dx_t$ is conserved by the dynamics and *not* simply dx_t. The factor $\exp[-w(x_t, t)]$ can be viewed as a metric determinant factor $\sqrt{g(x_t, t)}$, where $g(x_t, t)$ is the determinant of the metric tensor $G(x_t, t)$ obtained from $G(x_0, 0)$ via the coordinate transformation $x_0 \to x_t$. $G(x_0, 0)$, is the metric tensor describing the geometry of the space. Thus, at any time t, a nonunit metric determinant implies the existence of a nonzero dynamical compressibility. Note, the Jacobian governs the transformation

$$\sqrt{g(x_t, t)} dx_t = \sqrt{g(x_t, t)} J(x_t; x_0) dx_0 = \sqrt{g(x_0, 0)} dx_0, \tag{2.16}$$

and is, thus, a ratio of metric factors which, by definition, is unity, at $t = 0$ (see Appendix A).

In some cases, it may be possible to transform to a set of phase space coordinate where $\sqrt{g(x,t)}$ is unity or at least a constant. In this case, the phase space can be considered flat.[33] However, transformation to such a coordinate system may not be simple or may not exist for a given non-Hamiltonian system. The question of whether such transformations generally exist or not, although an interesting one, will not be addressed in the present work, as the general framework being introduced here is independent of this question. Indeed, the utility of Eq. (2.15) is that it permits an analysis of any non-Hamiltonian system to be carried out in an arbitrary set of coordinates. It should be noted that Eqs. (2.15) and (2.17) (see below) are formulated for a general phase space manifold and are, therefore, valid even if a transformation to a system where $\sqrt{g}$ is unity (or at least constant) does not exist and the phase space is not flat.[15–17] Indeed, a constant $\sqrt{g}$ is a necessary but not a sufficient condition for a Riemannian space to be a flat space. The more stringent condition is that the Riemann curvature tensor vanish, which will hold in any coordinate system. This condition will be met manifestly if, in a given coordinate system, all of the

components G_{ij} of the metric tensor are constant.[35] The complexity of these issues is avoided, however, by use of the formalism in Ref. 14.

C. The generalized Liouville equation

Next, consider an ensemble of systems evolving according to Eq. (2.8), described by a phase space distribution function $f(x,t)$. For a Hamiltonian system, $f(x,t)$ satisfies the standard Liouville equation, Eq. (2.3), which expresses the fact that $f(x,t)$ is a conserved probability distribution function. This equation is no longer valid for non-Hamiltonian systems. A covariant generalization was presented in Ref. 14 using modern techniques in differential geometry[36] as applied to dynamical systems,[15–17] and takes the form

$$\frac{\partial(f\sqrt{g})}{\partial t} + \nabla \cdot (f\sqrt{g}\dot{x}) = 0. \tag{2.17}$$

This equation was derived from the balance between the rate of decrease of the number of ensemble members in the phase space volume and the flux of members through the boundary surface taking into account the geometry of the space (number conservation). It is, therefore, valid for equilibrium as well as nonequilibrium ensembles generated by Hamiltonian or non-Hamiltonian systems. We have recently become aware of the fact that a generalization of the Liouville equation similar to Eq. (2.17) was written down (although without proof) some time ago by Ramshaw.[37]

Clearly, Eq. (2.17) reduces to Eq. (2.3) for Hamiltonian systems where $\sqrt{g(x,t)}=1$ and $\nabla_x \cdot \dot{x}=0$. As alluded to above, if a transformation to a frame where $\nabla_y \cdot \dot{y}=0$ exists with $y^k=y^k(x^1,\dots,x^n)$ then Eq. (2.17) reduces to Eq. (2.3) as can be verified by applying the transformation directly. Thus, Eq. (2.17) is valid when the phase space is not flat and remains valid in the limit in which it is flat. Again, the arguments given in Ref. 14 are important because they prove the validity of Eq. (2.17) in cases where the measure involves a nontrivial metric.

Note, that Eqs. (2.17) and (2.12) together imply that, even for a non-Hamiltonian system, $f(x,t)$ is conserved, i.e., $df/dt=0$. In general, the ensemble average of any property $A(x)$ is determined from the invariant measure and the ensemble distribution function $f(x,t)$,

$$\langle A \rangle_t = \frac{\int dx\,\sqrt{g(x,t)}A(x)f(x,t)}{\int dx\,\sqrt{g(x,t)}f(x,t)}. \tag{2.18}$$

In Ref. 14, it was further shown that the separation of $f(x,t)$ from the metric $\sqrt{g}$ is necessary in order to define a consistent *fine-grained* Gibbs entropy $S(t)$ $=-\int dx\,\sqrt{g(x,t)}f(x,t)\ln f(x,t)$ with respect to the invariant measure. This generalization of the Gibbs entropy satisfies the expected condition of a fine-grained entropy in a *closed* system, i.e., $dS/dt=0$.[38] However, it is clear from its definition that $S(t)$ need not correspond to any physically meaningful entropy. More detail is given in Sec. III B.

Consider the case where the ξ_i do not contain explicit time dependence and there are no external fields present. If, in addition, $\partial\sqrt{g}/\partial t=0$, then an equilibrium ensemble, for

which $\partial f/\partial t=0$ can be associated with Eqs. (2.8). From Eq. (2.18), it can be seen that these conditions are compatible with the stationarity of the ensemble average $\langle A \rangle$.

D. The generalized distribution function

Next, suppose that the set of dynamical equations possesses a set of n_c associated conservation laws or conserved quantities $\Lambda_k(x)$, $k=1,\dots,n_c$, which satisfy

$$\frac{d\Lambda_k}{dt}=0. \tag{2.19}$$

Thus, a trajectory generated by Eq. (2.8) will not sample the entire phase space, but a subspace determined by the intersection of the hypersurfaces $\{\Lambda_k(x)=C_k\}$, where C_k is a set of constants. Therefore, the microcanonical distribution function generated by the dynamical system can be constructed from a product of δ functions expressing the conservation laws,

$$f(x)=\prod_{k=1}^{n_c} \delta(\Lambda_k(x)-C_k). \tag{2.20}$$

It is possible to show, by substitution, that Eq. (2.20) satisfies the generalized Liouville equation, Eq. (2.17). In fact, Eq. (2.20) constitutes the complete solution for such a microcanonical ensemble, since all configurations that satisfy the conservation laws have equal probability of being visited by a trajectory.

It is important to note that a distribution constructed from a product of δ functions corresponding to an arbitrary *subset* of the conservation laws, also, satisfies the generalized Liouville equation

$$f_{\text{reduced}}(x)=\prod_{k=1}^{n_c'} \delta(\Lambda_k(x)-C_k), \tag{2.21}$$

where $n_c' \leq n_c$. If, $n_c' < n_c$, this solution will not properly describe the phase space distribution of a system with n_c conservation laws. Therefore, satisfying Eq. (2.17) is a necessary but not sufficient condition to guarantee that a particular phase space distribution function is generated by a given dynamical system. This illustrates the limitations of relying solely on the Liouville equation to determine the distribution function. Indeed, the true distribution must be consistent with *all* the conservation laws present.

E. The generalized phase space analysis

Given the above discussion, it is now possible to introduce a general procedure for constructing the partition function corresponding to the equilibrium ensemble generated by a non-Hamiltonian dynamical system satisfying the above conditions:

(1) Determine *all* the conservation laws satisfied by the equations of motion. The distribution function $f(x)$ will then be given by Eq. (2.20).

(2) Using the conservation laws and the equations of motion, identify and eliminate linearly dependent variables/solutions. That is, if $x_2(t)=Cx_1(t)$, where C is a constant then $x_2(t)$ must be removed from the formal analysis of the

dynamical system. (Note, however, that such dependencies form a set of conservation laws and can also be eliminated in steps 4 and 5 below if they are not eliminated in this step.) Driven or trivial or uncoupled variables must also be eliminated in the formal analysis. That is, if $\dot{x}_a = \xi_a(x_a)$ and $\dot{x}_b = \xi_b(x_a, x_b)$ with x_a of primary importance, and there only exists conservation laws of the form $\Lambda_k(x_a) = 0$ and $\Lambda_{k'}(x_b) = 0$, then x_b must be eliminated, as the phase space distribution of x_a is, in no way, affected by x_b. This step will identify variables of lesser physical importance, e.g., center of mass motion, in complex systems. Idealized systems, such as separable systems, need to be treated as special cases.

(3) Calculate the phase space compressibility, $\nabla_{x'} \cdot \dot{x}'$, of the remaining dynamical system, $\dot{x}' = \tilde{\xi}(x')$ (having eliminated trivial variables and linear dependent solutions as described in step 2). Using the compressibility, determine the phase space metric, $\sqrt{g(x')}$ and generate the invariant volume element, $\sqrt{g(x')} dx'$.

(4) The microcanonical partition function can now be constructed using

$$\Omega(C_1, ..., C_{n_c}) = \int dx' \sqrt{g(x')} \prod_{k=1}^{n_c} \delta(\Lambda_k(x') - C_k). \tag{2.22}$$

Note that, as in Eq. (2.5), the partition function is invariant under coordinate transformations $x'_0 \rightarrow x'_t$ and can therefore be computed in terms of the coordinates at *any* time t.

(5) If Eq. (2.8) corresponds to a system with an extended phase space, then Eq. (2.22) must be integrated over the extended phase space variables in order to determine the distribution function sampled by the physical variables.

The theoretical results of step $1-5$ should always be tested numerically on a set of model problems. Step 5 assumes ergodicity on the x' phase space subject to the conservation laws, and steps $1-4$ are merely a necessary but not sufficient condition to ensure ergodicity. In particular, steps $1-4$ do not address more complex issues of ergodicity such as arise when there are large potential energy barriers. However, steps $1-4$ are sufficient for the problems studied here. It is also important to note that only an exceedingly small number of systems can be shown formally to be ergodic and it is unlikely that ergodicity can be shown analytically for the complex set of systems of interest in chemical physics.

III. SPECIFIC ADVANTAGES AND CONNECTION TO PRIOR WORK

Given that a new formalism has been derived, it is first important to examine and highlight the differences between the new formalism and older work as well as to elucidate the general deficiencies of older formalisms. It is also important to give a series of specific illustrative examples that either have led to failure in previous formalisms or stringently test the new formalisms. These examples must then be worked out in complete detail and compared to supporting numerical calculations (see Secs. IV–VI).

A. Other forms of the generalized Liouville equation

Of primary importance is the generalized Liouville equation, Eq. (2.17). Although a rigorous derivation of this equation was presented in Ref. 14, the line of reasoning that leads to Eq. (2.17) is as follows:

(1) Equation (2.15) implies that there is a measure conservation law that, most generally, involves a nontrivial metric. This suggests that phase space should be carefully treated using the general rules of the geometry of manifolds.
(2) Based on item 1, the Liouville equation was rederived using the mathematical techniques of differential geometry;[36]
(3) The rules of differential geometry require that the phase space distribution function $f(x,t)$ be kept separate from the phase space metric $\sqrt{g}$ and, therefore, leads naturally to Eq. (2.17) which contains both a metric and a distribution function.

Existing formalisms for non-Hamiltonian systems are based on a generalized Liouville equation of the form

$$\frac{\partial \tilde{f}}{\partial t} + \dot{x} \cdot \nabla_x \tilde{f} = -\tilde{f} \nabla_x \cdot \dot{x}, \tag{3.1}$$

which is derived *assuming* a flat phase space. In Eq. (3.1), the notation $\tilde{f}$ is used to distinguish it from f in Eq. (2.17). Clearly, Eq. (3.1) is related to Eq. (2.17) through the identification $\tilde{f} = \sqrt{g} f$. Therefore, Eq. (3.1) is not incorrect, but is incomplete.

The more mathematically precise and fundamental form, Eq. (2.17), has a powerful advantage. It allows one to directly construct the microcanonical partition function in a manner analogous to the Hamiltonian case. Because Eq. (3.1) is incomplete, its use to extract the partition function is awkward and is not rigorous. What is generally done is to postulate a form for $\tilde{f}$ and show that this form satisfies Eq. (3.1). Such an *ad hoc* procedure usually misses important information and often leads to incomplete solutions. Specific failures of this simplistic approach are discussed in detail below.

In order to demonstrate this more generally, note that Eq. (3.1) admits any general solution of the form $\tilde{f}(x,t) = f_0(x,t) f_1(x,t)$, where $f_0(x,t)$ is any function satisfying $df_0/dt = 0$. Once this fact is recognized, then it is clear that Eq. (3.1) reverts to Eq. (2.17) since, in Eq. (2.17), $f(x,t)$ satisfies $df/dt = 0$. In other words, Eq. (3.1) alone cannot determine the function $f_0(x,t)$ since it simply cancels out. The example to be shown in Sec. IV A [see Eqs. (4.17)–(4.20)] is just one of numerous examples that have appeared in the literature in which an incomplete solution was treated as the *full* solution of Eq. (3.1) and incorrect phase space distributions were, consequently, obtained. By contrast, the formalism presented in this work shows how to determine the phase space metric and how to construct the phase space distribution so that a full and general solution to Eq. (2.17) is obtained.

Other authors have suggested working only in coordinate systems in which $\sqrt{g}$ is constant,[31] in which case, the

deficiencies of Eq. (3.1) are bypassed. However, this transformation may not exist or may simply be nontrivial to employ. Our covariant formulation also permits the use of such coordinate systems but does not require them.

B. Defining the Gibbs entropy for closed systems

As a specific example of the failure of the improper use of Eq. (3.1), consider the case of the fine-grained Gibbs entropy. In a *closed* system, the Gibbs entropy should satisfy the expected condition for a fine-grained entropy i.e., $dS/dt = 0$.[38] In Ref. 14, it was shown that the separation of $f(x,t)$ from the metric $\sqrt{g}(x,t)$ is necessary in order to define a *fine-grained* Gibbs entropy $S(t)$ $-\int dx \sqrt{g(x,t)} f(x,t) \ln f(x,t)$ with respect to the invariant measure such that $dS/dt = 0$ in all coordinate systems. The standard form of the Liouville equation led other workers to define a coordinate system dependent fine grained entropy, $\widetilde{S}(t) = -\int dx \widetilde{f}(x,t) \ln \widetilde{f}(x,t)$, whose time derivative only vanishes in coordinate systems in which $\sqrt{g} = $ constant. Although it is clear that for an arbitrary set of equations of motion the Gibbs entropy need not correspond to a physically meaningful quantity, the fact that the latter definition leads to $d\widetilde{S}/dt \neq 0$, in some coordinate systems, has given rise to erroneous speculation about the nature of non-Hamiltonian phase space. Clearly, the physics cannot depend on the choice of coordinate systems. Note, the coordinate independent form is the appropriate choice for performing information theory analyses on dynamical systems (see Ref. 39).

C. Specific examples and failures of previous analyses

The remainder of this paper will be devoted to applying the above procedure to several commonly used non-Hamiltonian dynamical systems and demonstrating the failures of older analyses. In particular, canonical (NVT) and isothermal–isobaric (NPT) extended system methods, the isokinetic method, and methods for treating systems subject to holonomic constraints will be considered:

(1) The canonical and isothermal–isobaric ensembles are useful ensembles. Therefore, various extended system molecular dynamics methods have been designed to treat them. However, in formulating these methods, the use of the standard Liouville equation, Eq. (3.1), has led to incorrect definitions of the ensemble produced by the dynamics. That is, rather than using a generalized microcanonical partition function [see Eq. (2.22)], a distribution function $\widetilde{f}$ is postulated, shown to satisfy Eq. (3.1), and the equations of motion pronounced correct (cf. Refs. 40 and 41). Often, the postulated form is incomplete in the sense of Eq. (2.21) and does not properly describe the distribution generated by the dynamics, i.e., the equations of motion may generate a distribution that is not of the predicted form. It is demonstrated in great detail in Secs. IV–V that the new phase space picture succeeds in predicting complex distribution functions where these older methods fail.

(2) It will be seen in Sec. IV that the extended system equations of motion for the canonical and isothermal isobaric ensemble possess relatively simple metrics. It is, therefore,

possible to define a simple transformation to a coordinate system where $\sqrt{g} = $ constant. For this reason, we will examine the isokinetic equations of motion, derived from Gauss' principle of least constraint,[1] which have a nontrivial metric and show that the new non-Hamiltonian phase space formalism leads to the correct isokinetic partition function.

(3) Systems with holonomic constraints are of great interest in MD. These are commonly used to increase time steps by freezing the motion of fast variables whose dynamics is fairly uncoupled from the rest of the system. Years of controversy about the distribution function produced by these MD methods were resolved by Fixman[24] by careful and intricate changes of variables in generalized coordinates and clarified more recently by Ciccotti et al.[23,25–28] in Cartesian coordinates. Using our generalized non-Hamiltonian phase space approach, the original variables can be employed to predict straightforwardly the resulting ensemble, which leads to a substantial simplification of the derivation.[42]

IV. THE CANONICAL AND ISOKINETIC ENSEMBLES

A. The canonical ensemble

Consider an N-particle system in d dimensions with Cartesian positions $\mathbf{r} \equiv \{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$ and momenta $\mathbf{p} \equiv \{\mathbf{p}_1, \ldots, \mathbf{p}_N\}$. The canonical ensemble is described by the phase space distribution function

$$f(\mathbf{p},\mathbf{r}) = \frac{C_N / h^{dN}}{Q(N,V,T)} e^{-\beta H(\mathbf{p},\mathbf{r})} \tag{4.1}$$

and corresponding partition function

$$Q(N,V,T) = \frac{C_N}{h^{dN}} \int d^N \mathbf{p} \int_{D(V)} d^N \mathbf{r} e^{-\beta H(\mathbf{p},\mathbf{r})}, \tag{4.2}$$

where $H(\mathbf{p},\mathbf{r})$ is the Hamiltonian of the physical system, $\beta = 1/kT$, $D(V)$ is the spatial domain defined by the containing volume, V, C_N is a combinatorial factor, and h is Planck's constant. (For simplicity the prefactor C_N / h^{dN} will be dropped throughout the remainder of the paper.) Any dynamical scheme that seeks to generate canonical distributed positions and momenta must produce Eqs. (4.1) and (4.2), modulo constant prefactors.

B. The Nosé–Hoover algorithm

It has been postulated that the following non-Hamiltonian dynamical system:

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i},$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \frac{p_\eta}{Q} \mathbf{p}_i,$$

$$\dot{\eta} = \frac{p_\eta}{Q}, \tag{4.3}$$

$$\dot{p}_\eta = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} - LkT,$$

where the forces $\mathbf{F}_i$ are derived from an N-particle potential $\phi(\mathbf{r}_1,...,\mathbf{r}_N,V)$ by $\mathbf{F}_i=-\nabla_{\mathbf{r}_i}\phi$ and L is a parameter, is capable of generating a canonical distribution in the physical degrees of freedom.[2]

Equations (4.3) contain two nonphysical variables, η and p_η, giving an overall phase space dimension of $2dN+2$, where d is the number of spatial dimensions. These new variables can be regarded as a "thermostat" which controls the fluctuations in the total kinetic energy of the system around the average kinetic energy, i.e., $LkT/2$. The reader familiar with the MD literature will recognize these as the Nosé–Hoover equations, which are based on the original Hamiltonian formulation by Nosé and Klein.[43,44] The parameter, Q, determines the time scale on which the thermostat evolves and takes the form

$$Q=LkT\tau^2. \tag{4.4}$$

Here, τ is a time scale relevant to the physical system. The parameter L will be determined in the analysis.

The conditions under which Eqs. (4.3) can generate a canonical distribution in the physical variables will be analyzed by applying the procedure of Sec. II. First, all conservation laws must be identified. The most basic conserved quantity is the total "energy"

$$H'=\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i}+\phi(\mathbf{r}_1,...,\mathbf{r}_N,V)+\frac{p_\eta^2}{2Q}+LkT\eta$$

$$=H(\mathbf{p},\mathbf{r})+\frac{p_\eta^2}{2Q}+LkT\eta=C_1, \tag{4.5}$$

where $H(\mathbf{p},\mathbf{r})$ is the physical Hamiltonian. Assuming Eq. (4.5) is the only conserved quantity, then according to the procedure defined in Sec. II, the compressibility must be calculated and is given by $\kappa(x)=\nabla_x\cdot\dot{x}=\Sigma_i\nabla_{\mathbf{p}_i}\cdot\dot{\mathbf{p}}_i=-dNp_\eta/Q=-dN\dot{\eta}$. Thus, the metric is $\sqrt{g}=\exp(dN\eta)$. The microcanonical partition function at a given temperature T can be constructed using $\sqrt{g}$ and the energy conservation condition,

$$\Omega_T(N,V,C_1)=\int d^N\mathbf{p}\int_{D(V)}d^N\mathbf{r}\int dp_\eta d\eta e^{dN\eta}\delta$$

$$\times\left(H(\mathbf{p},\mathbf{r})+\frac{p_\eta^2}{2Q}+LkT\eta-C_1\right), \tag{4.6}$$

where the T subscript indicates that the microcanonical partition function depends parametrically on the temperature, T.

The distribution function in the physical subspace can now be obtained by integrating over η and p_η. Using the δ function to perform the integration over η requires that

$$\eta=\frac{1}{LkT}\left(C_1-H(\mathbf{p},\mathbf{r})-\frac{p_\eta^2}{2Q}\right). \tag{4.7}$$

Substitution of this result into Eq. (4.6) gives

$$\Omega_T(N,V,C_1)=\frac{e^{\beta dNC_1/L}}{LkT}\int dp_\eta e^{-\beta dNp_\eta^2/2QL}$$

$$\times\int d^N\mathbf{p}\int_{D(V)}d^N\mathbf{r}e^{-\beta dNH(\mathbf{p},\mathbf{r})/L}$$

$$\propto Q(N,V,T), \tag{4.8}$$

which is the canonical distribution function (modulo constant prefactors) provided $L=dN$ as might be expected. This demonstrates that the Nosé–Hoover equations are capable of generating a canonical distribution in the physical subsystem variables when H' is the *only* conserved quantity.

It is worth noting that for simple non-Hamiltonian systems such as the Nosé–Hoover algorithm, it is possible to eliminate the metric factor by reformulating the equations of motion in terms of a variable $\eta'=\exp(dN\eta)$. In this case, the equations of motion will be incompressible, and the metric factor $\sqrt{g}$ will be constant. Of course, such an elementary transformation may not exist for other non-Hamiltonian system (see, e.g., Sec. III D). Therefore, in order to illustrate the generality of the present approach, we have used the variable η instead of η' in the proceeding examples.

Consider the case in which there are no external forces on the system, so that $\Sigma_i\mathbf{F}_i=0$. As was pointed about by Nosé,[40] there are d additional conservation laws satisfied by Eqs. (4.3), which take the form

$$\mathbf{P}e^\eta=\mathbf{K}, \tag{4.9}$$

where $\mathbf{P}=\Sigma_{i=1}^{N}\mathbf{p}_i$ is the center-of-mass momentum of the system and $\mathbf{K}$ is an arbitrary constant vector in d dimensions. Equation (4.9) can be verified by taking the time derivative, explicitly, and using the equations of motion and the definition of $\mathbf{P}$ as the sum over all particle momenta to simplify.

According to the procedure of Sec. II, driven and linearly dependent variables must be eliminated in order to perform a proper formal analysis. The components of $\mathbf{P}$ are linearly dependent, $P_\alpha(t)=C_{\alpha\beta}P_\beta(t)$ with $C_{\alpha\beta}$ constant and $\alpha,\beta=1,...,d$. Thus, $d-1$ components of the center-of-mass momenta must be eliminated. Second, the center-of-mass positions $\mathbf{R}$ are driven variables (their dynamics does not effect other variables, and they do not contribute to a nontrivial conserved quantity) and must also be eliminated in the formal analysis. Thus, a canonical transformation to a set of relative coordinates and momenta $\{\mathbf{p}',\mathbf{P},\mathbf{r}',\mathbf{R}\}$ is introduced, in which $\mathbf{R}$ and $\mathbf{P}$ are explicit variables, and the equations of motion for the $\mathbf{P}$, written in terms of the single independent variable $P=\sqrt{\Sigma_\alpha P_\alpha^2}$. This procedure yields the following transformed equations of motion:

$$\dot{\mathbf{r}}_i'=\frac{\mathbf{p}_i'}{m_i'},\quad \dot{\mathbf{p}}_i'=\mathbf{F}_i'-\frac{p_\eta}{Q}\mathbf{p}_i',\quad \dot{P}=-\frac{p_\eta}{Q}P,$$

$$\dot{\eta}=\frac{p_\eta}{Q},\quad \dot{p}_\eta=\sum_{i=1}^{N-1}\frac{\mathbf{p}_i'^2}{m_i'}+\frac{P^2}{M}-LkT. \tag{4.10}$$

These equations have compressibility, $\kappa=-[d(N-1)+1]\dot{\eta}$, metric $\sqrt{g}=\exp\{[d(N-1)+1]\eta\}$, and two conserved quantities, $H'=H(\mathbf{p}',\mathbf{r}',P)+p_\eta^2/2Q+LkT\eta$, and $K=Pe^\eta$. Note the fact that $H(\mathbf{p},\mathbf{r})\equiv H(\mathbf{p}',\mathbf{r}',P)$ has been employed.

The conservation laws and the metric can now be used to construct the microcanonical partition function,

$$\Omega_T(N,V,C_1,C_2) = \int d^{N-1}\mathbf{p}' \, dP \int_{D(V)} d^{N-1}\mathbf{r}'$$

$$\times \int dp_\eta d\eta e^{[d(N-1)+1]\eta}$$

$$\times \delta\left(H(\mathbf{p}',\mathbf{r}',P) + \frac{p_\eta^2}{2Q} \right.$$

$$\left. + LkT\eta - C_1 \right) \delta(e^\eta P - C_2). \quad (4.11)$$

The distribution function in the physical subspace is obtained by integrating over η and p_η. Using the δ function $\delta(e^\eta P - C_2)$ to perform the integration over η, one obtains

$$\Omega_T(N,V,C_1,C_2) = \frac{1}{C_2} \int d^{N-1}\mathbf{p}' \int dP \int_{D(V)} d^{N-1}\mathbf{r}'$$

$$\times \int dp_\eta \left(\frac{C_2}{P} \right)^{d(N-1)+1}$$

$$\times \delta\left(H(\mathbf{p}',\mathbf{r}',P) + \frac{p_\eta^2}{2Q} \right.$$

$$\left. + LkT \ln\frac{C_2}{P} - C_1 \right). \quad (4.12)$$

Next, the energy δ function can be used to perform the integration over p_η to yield

$$\Omega_T(N,V,C_1,C_2) = \frac{\sqrt{2Q}}{C_2} \int d^{N-1}\mathbf{p}' \int dP \int_{D(V)} d^{N-1}\mathbf{r}'$$

$$\times \left(\frac{C_2}{P} \right)^{d(N-1)+1}$$

$$\times \frac{1}{\sqrt{C_1 - H(\mathbf{p}',\mathbf{r}',P) - LkT \ln(C_2/P)}}. \quad (4.13)$$

Equation (4.13) clearly does not describe a canonical ensemble (as discussed by Cho and Joannapolous[45] and by Martyna[46]). Moreover, the phase space distribution function given in Eq. (4.13) may contain forbidden regions or islands and sharp boundaries corresponding to negative or zero argument of the square root. It is worth noting, however, that for the special choice $C_2 = 0$, corresponding to the choice $P(0) = 0$, the same analysis can be shown to lead to an $(N-1)VT$ ensemble distribution.

As a concrete illustration of Eq. (4.13), consider the case of a free particle in one spatial dimension coupled to a Nosé–Hoover thermostat. Here, the equations of motion take the form

$$\dot{p} = -\frac{p_\eta}{Q}p \quad \dot{\eta} = \frac{p_\eta}{Q} \quad \dot{p}_\eta = \frac{p^2}{m} - kT, \quad (4.14)$$

where the physical Hamiltonian is just $H(p) = p^2/2m$. Setting $d = 1$ and $N = 1$ in Eq. (4.13) gives a momentum distribution function of the form

$$f(p) = \frac{\sqrt{2Q}}{\sqrt{p^2(C_1 - (p^2/2m) + kT \ln(p/C_2))}}. \quad (4.15)$$

Equation (4.15) is precisely the momentum distribution obtained if Eqs. (4.14) are integrated numerically, as is shown in Fig. 1(a). In this and all subsequent numerical examples, the integration methods in Ref. 47 are employed. As might be expected in this simple problem, the trajectory is ergodic. It samples all of the phase space available to it, on the correct hypersurface (a line). It generates, therefore, the predicted momentum distribution function. However, the distribution is not canonical. The rather peculiar form of Eq. (4.15) is a consequence of the two conservations laws,

$$H' = \frac{p^2}{2m} + \frac{p_\eta^2}{2Q} + kT\eta = C_1,$$
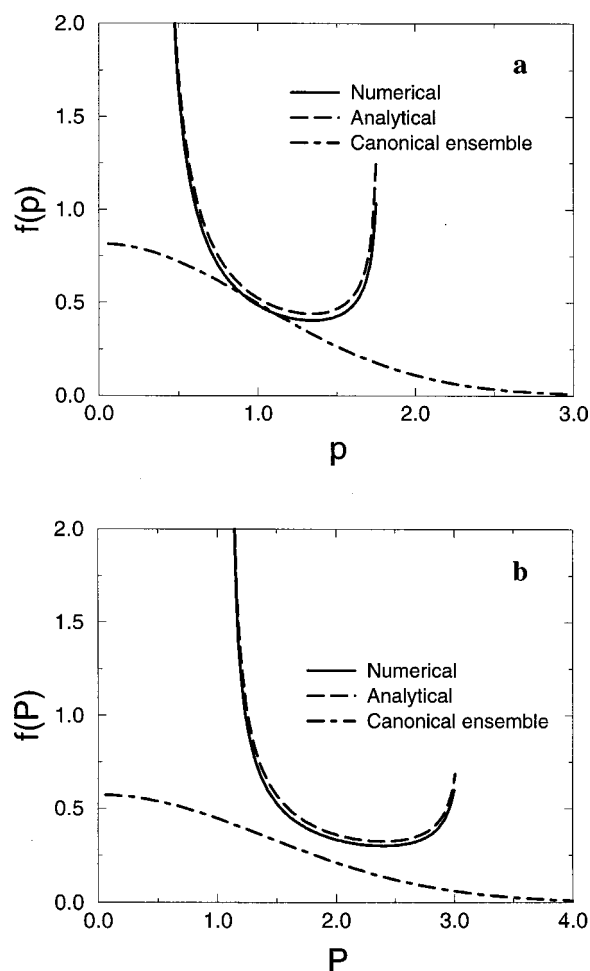
$$(4.16)$$

$$K \equiv pe^\eta = C_2.$$

FIG. 1. (a) The momentum distribution function for a one-dimensional free particle coupled to a Nosé–Hoover thermostat (solid line) [$m=1$, $kT=1$, $p(0)=1$, $q(0)=0$, $Q=1$, $p_\eta(0)=1$ with a time step $\Delta t = 0.05$] compared to the analytical result (dashed line) and the canonical ensemble distribution (dot dashed line). (b) The same for the center-of-mass momentum distribution for two one-dimensional free particles [$m_1 = m_2 = 1$, $kT=1$, $p_1(0) = p_2(0) = 1$, $x_1(0) = 0$, $x_2(0) = 0.5$, $Q=2$, $p_\eta(0) = \sqrt{2}$].

Figure 1(b) shows the distribution function of the center-of-mass momentum obtained for two free particles coupled to a single Nosé–Hoover thermostat.

Having discussed these pedagogical examples, we will now show how the incomplete version of the Liouville equation, Eq. (3.1), can lead to an incorrect prediction of the phase space sampled by Eqs. (4.3). For the Nosé–Hoover equations, (4.3), Eq. (3.1) becomes

$$\frac{d\tilde{f}}{dt} = dN \frac{p_\eta}{Q} \tilde{f},$$

(4.17)

$$\frac{d\ln\tilde{f}}{dt} = dN \frac{p_\eta}{Q}.$$

Note, however, that the quantity

$$H'' = H(\mathbf{p},\mathbf{r}) + \frac{p_\eta^2}{2Q}$$

(4.18)

satisfies

$$\frac{dH''}{dt} = -LkT \frac{p_\eta}{Q}.$$

(4.19)

Therefore, equating the two time derivatives, and setting $L = dN$, one would be led to conclude that[40]

$$\ln\tilde{f} = -\beta H'' + \text{const},$$

$$\tilde{f} \propto \exp(-\beta H'') = \exp\left[-\beta\left(\frac{p_\eta^2}{2Q} + H(\mathbf{p},\mathbf{r})\right)\right]$$

(4.20)

was generate by the dynamics under all circumstances.

However, it has been made clear that if more than one conservation law exists, linear dependent solutions are present and/or driven variables remain unidentified, the above procedure will fail to predict the correct distribution. Again, satisfying the generalized Liouville equation is a necessary but not sufficient condition to guarantee that a given distribution function is, in fact, generated by a dynamical system. Note that, corresponding to Eqs. (4.14), $f(p,p_\eta,\eta) = \delta(H(p) + p_\eta^2/2Q + kT\eta - C_1)\delta(p\exp(\eta) - C_2)$, which together with $\sqrt{g} = \exp(\eta)$, leads to the correct distribution actually generated by the dynamics (not a canonical distribution) also satisfies the generalized Liouville equation.

C. The Nosé–Hoover chain algorithm

The difficulties resulting from the presence of multiple conservation conditions in the Nosé–Hoover system can be eliminated via the use of the Nosé–Hoover chain (NHC) method.[46,48] Here, the kinetic energy fluctuations of the thermostat variable are controlled by coupling it to another thermostat variable. The kinetic energy fluctuations of the second thermostat are, in turn, controlled by coupling to a third thermostat, and so on, to form a chain of M thermostats. It will be shown below how the new coupling (the Nosé–Hoover "chain" thermostatting mechanism) leads to a more general canonical dynamics method.

The Nosé–Hoover chain method can be expressed in terms of the following non-Hamiltonian dynamical system:

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i},$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \frac{p_{\eta_1}}{Q_1}\mathbf{p}_i,$$

$$\dot{\eta}_k = \frac{p_{\eta_k}}{Q_k} \quad k = 1,...,M,$$

$$\dot{p}_{\eta_1} = \left[\sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} - LkT\right] - \frac{p_{\eta_2}}{Q_2}p_{\eta_1},$$

(4.21)

$$\dot{p}_{\eta_k} = \left[\frac{p_{\eta_{k-1}}^2}{Q_{k-1}} - kT\right] - \frac{p_{\eta_{k+1}}}{Q_{k+1}}p_{\eta_k} \quad k = 2,...,M-1,$$

$$\dot{p}_{\eta_M} = \left[\frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - kT\right].$$

It was shown in Ref. 49 that an optimal choice for the thermostat parameters $Q_1,...,Q_M$ is

$$Q_1 = LkT\tau^2,$$

(4.22)

$$Q_k = kT\tau^2 \quad k = 2,...,M.$$

Equations (4.21) have the conserved energy

$$H' = H(\mathbf{p},\mathbf{r}) + \sum_{k=1}^M \frac{p_{\eta_k}^2}{2Q_k} + LkT\eta_1 + kT\sum_{k=2}^M \eta_k.$$

(4.23)

Assuming this to be the only conservation laws, there are no linear dependencies. However, only η_1 and the thermostat center $\eta_c = \Sigma_{k=2}^M \eta_k$ are independently coupled to the dynamics. Other linear combinations of thermostat variables $k>2$ are driven or trivial variables. Thus, the compressibility of Eqs. (4.21) is

$$\nabla_x \cdot \dot{x} = -dN \frac{p_{\eta_1}}{Q_1} - \sum_{k=2}^M \frac{p_{\eta_k}}{Q_k} = -dN\dot{\eta}_1 - \dot{\eta}_c,$$

(4.24)

and the phase space metric is

$$\sqrt{g} = \exp[dN\eta_1 + \eta_c].$$

(4.25)

In this case, the proof that Eqs. (4.21) generate a canonical distribution is analogous to Eqs. (4.6)–(4.8) and, therefore, will not be repeated here.

In a system where the forces sum to zero, the momentum conservation condition is

$$\mathbf{K} = \mathbf{P}e^{\eta_1},$$

(4.26)

where $\mathbf{P}$ is the center-of-mass momentum. Thus, as in the Nosé–Hoover ($M=1$) example, the $\mathbf{P}$ are linearly dependent and the $\mathbf{R}$ are driven variables. Following the previous analysis, the metric becomes

$$\sqrt{g} = \exp[(dN-d+1)\eta_1 + \eta_c]$$

(4.27)

and the microcanonical partition function can be written as

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$$\Omega_T(N,V,C_1,C_2) = \int d^{N-1}\mathbf{p}' \, dP \int_{D(V)} d^{N-1}\mathbf{r}'$$

$$\times \int d\eta_1 \, d\eta_c \int d^M p_\eta e^{[(dN-d+1)\eta_1 + \eta_c]}$$

$$\times \delta(H'-C_1)\delta(Pe^{\eta_1}-C_2).$$

It is possible to integrate over the variable η_1 using the δ function $\delta(Pe^{\eta_1}-C_2)$ to yield

$$\Omega_T(N,V,C_1,C_2) = \frac{1}{C_2} \int d^{N-1}\mathbf{p}' \, dP \int_{D(V)} d^{N-1}\mathbf{r}'$$

$$\times \int d^M p_\eta \int d\eta_c \left(\frac{C_2}{P}\right)^{d(N-1)+1} e^{\eta_c}$$

$$\times \delta\left(H(\mathbf{p}',\mathbf{r}',P) + \sum_{k=1}^{M} \frac{p_{\eta_k}^2}{2Q_k} \right.$$

$$\left. + LkT \ln \frac{C_2}{P} + kT\eta_c - C_1 \right). \quad (4.28)$$

Finally, using η_c to integrate over the energy δ function, one obtains

$$\Omega_T(N,V,C_1,C_2) = \frac{\exp(C_1/kT)}{C_2 kT} \int d^M p_\eta$$

$$\times \exp\left[-\beta \sum_{k=1}^{M} \frac{p_{\eta_k}^2}{2Q_k} \right] \int d^{N-1}\mathbf{p}' \, dP$$

$$\times \int_{D(V)} d^{N-1}\mathbf{r}' e^{-\beta H(\mathbf{p}',\mathbf{r}',P)}$$

$$\times \left(\frac{P}{C_2}\right)^{L-d(N-1)-1}. \quad (4.29)$$

If $L=dN$, Eq. (4.29) is the correct canonical distribution in all relevant phase space variables modulo a constant prefactor.

The center-of-mass positions and angular components of the center-of-mass momentum do not explicitly appear in Eq. (4.29), as the Hamiltonian, $H(\mathbf{p}',\mathbf{r}',P)$ does not depend on these variables in this case, and they are, therefore, not formally part of the phase space. Including them would only change the overall constant prefactor, which does not affect any physical phase space average.

Consider, again, the example of a free particle in one spatial dimension now coupled to a Nosé–Hoover chain of length $M=3$. Figure 2(a) shows that the Nosé–Hoover chain method is capable of reproducing the correct canonical momentum distribution for $p \geq 0$ (for a free particle, the equation of motion $\dot{p} = -p_{\eta_1} p/Q_1$ is invariant under a transformation $p \to -p$ and hence p cannot change sign).

For two free particles, the center-of-mass momentum distribution is not correctly reproduced because of an additional conservation law on the relative momentum, $p = (m_2 p_1 - m_1 p_2)/M$, which takes the form

$$pe^\eta = k, \quad (4.30)$$

which implies that the relative momentum is linearly dependent on the center-of-mass momentum, i.e., $p = \lambda P$ [see Fig. 2(b)]. In this case, it can be shown that the momentum distribution obtained is

$$f(P) = P \exp\left[-\frac{1}{kT}\left(\frac{P^2}{2M} + \frac{\lambda^2 P^2}{2\mu} \right) \right]. \quad (4.31)$$

This artifact can be eliminated by adding a suitable potential coupling to the particles (or employing tensorial thermostatting methods[46]). Consider the same two-particle system with a harmonic potential $\phi(x_1,x_2) = k(x_1-x_2)^2/2$. In this case, Eq. (4.30) no longer holds, and the center-of-mass distribution obtained is the correct canonical distribution, shown in Fig. 3(a). In addition, the canonical distribution of the relative coordinate x_1-x_2 is also correctly generated, as shown in Fig. 3(b).
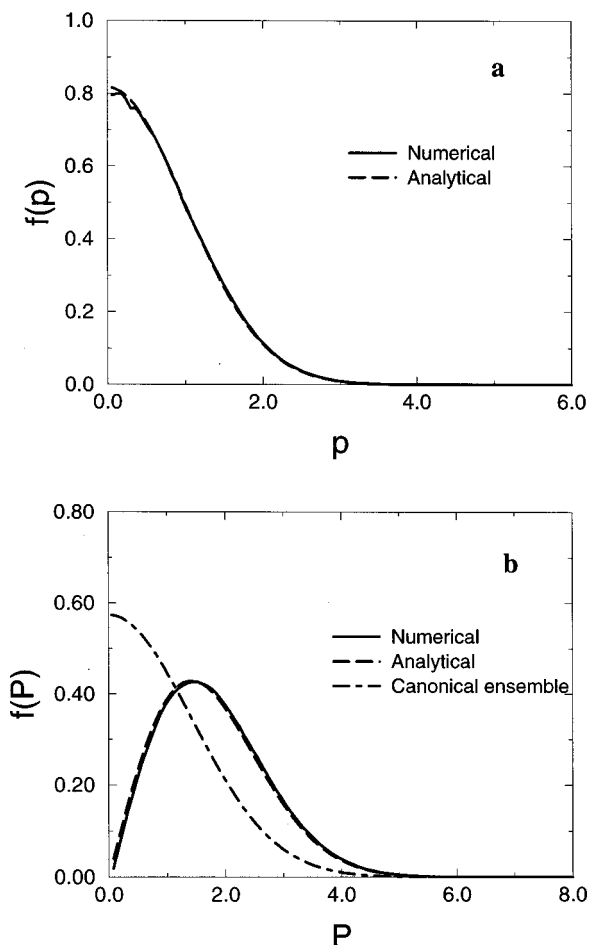

FIG. 2. (a) The momentum distribution function for a one-dimensional free particle coupled to a Nosé–Hoover chain of $M=3$ (solid line) [$m=1$, $kT=1$, $p(0)=1$, $q(0)=0$, $Q_i=1$, $p_{\eta_1}(0)=p_{\eta_3}(0)=1$, $p_{\eta_2}(0)=-1$ with a time step $\Delta t=0.05$] compared to the analytical distribution (dashed line). In this case, the analytically predicted distribution is identical to the canonical ensemble distribution. (b) The center-of-mass momentum distribution for two one-dimensional free particles (solid line) [$m_1=m_2=1$, $kT=1$, $p_1(0)=0.8$, $p_2(0)=1.166$, $x_1(0)=0$, $x_2(0)=0.5$, $Q_1=2$, $Q_2=Q_3=1$, $p_{\eta_i}(0)=(-1)^{i-1}\sqrt{Q_i}$] compared to the analytical result (dashed line) and the canonical ensemble distribution (dot dashed line).
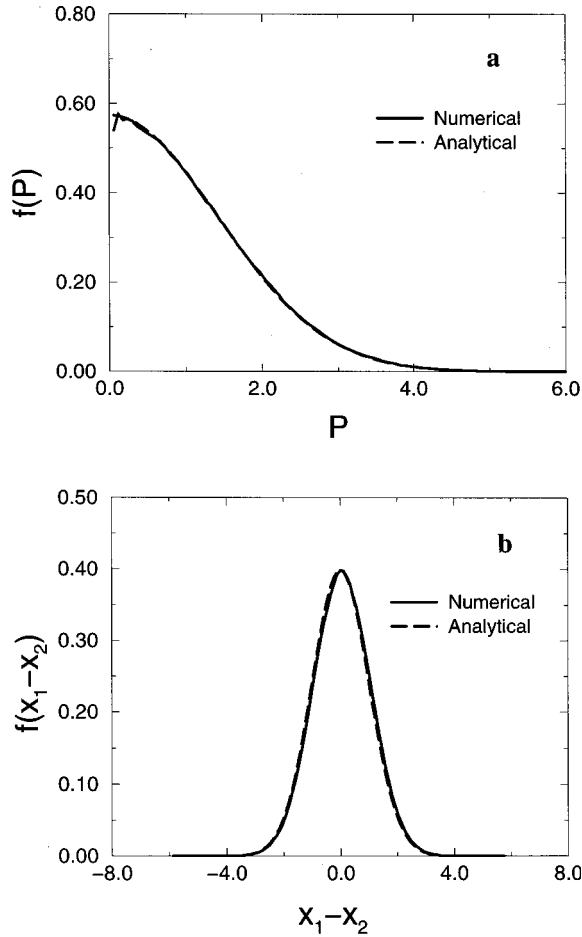
FIG. 3. (a) The center-of-mass momentum distribution function for a one-dimensional, two-particle system coupled to a harmonic potential with k $=1$ (see text) generated by the Nosé–Hoover chain dynamics (solid line) $[p_1(0)=0.8,\ p_2(0)=1.166,\ x_1(0)=x_2(0)=0$, and the same initial condition for the thermostat variables as in Fig. 2 with a time step $\Delta t=0.05]$ compared to the analytical distribution (dashed line). (b) The same for the relative coordinate distribution function. In both cases, the analytically predicted distribution is identical to the canonical ensemble distribution.

D. The isokinetic ensemble

The equations of motion for the isokinetic or constant kinetic energy ensemble are introduced as an example of a non-Hamiltonian system for which no transformation is generally known which restores incompressible dynamics. The isokinetic equations of motion generate a true canonical configurational distribution $P(\mathbf{r})\propto\exp(-\beta\phi(\mathbf{r}))$ as has been discussed in detail in Ref. 10, however, the total kinetic energy is constrained to be a constant,

$$\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i}=\frac{(dN-1)}{2}kT. \tag{4.32}$$

The fact that the constant is equal to $(dN-1)kT$ reflects the fact that there is a constraint in the system which reduces the number of degrees of freedom by one (see below).

The isokinetic condition can be enforced via Gauss' principle of least constraint,[1,7,10] in which Hamilton's equations of motion are supplemented by the addition of an appropriate force,

$$\dot{\mathbf{r}}_i=\frac{\mathbf{p}_i}{m_i}$$

$$\dot{\mathbf{p}}_i=\mathbf{F}_i-\alpha\mathbf{p}_i. \tag{4.33}$$

The Lagrange multiplier α is a function of the phase space variables and is determined by the minimum projection of the force $\mathbf{F}_i$ onto the surface of constraint. Its specific form is obtained by differentiating Eq. (4.32) once with respect to time and substituting the expression for $\dot{\mathbf{p}}$ into the result

$$\sum_{i=1}^{N}\frac{\mathbf{p}_i}{m_i}\cdot\dot{\mathbf{p}}_i=0,$$

$$\sum_{i=1}^{N}\frac{\mathbf{p}_i}{m_i}\cdot[\mathbf{F}_i-\alpha\mathbf{p}_i]=0, \tag{4.34}$$

$$\alpha=\frac{\sum_{i=1}^{N}\mathbf{F}_i\cdot\mathbf{p}_i/m_i}{\sum_{j=1}^{N}\mathbf{p}_j^2/m_j}.$$

The expression for α can be inserted into the equations of motion to yield a non-Hamiltonian dynamical system of the form

$$\dot{\mathbf{r}}_i=\frac{\mathbf{p}_i}{m_i}$$

$$\dot{\mathbf{p}}_i=\mathbf{F}_i-\left[\frac{\sum_{j=1}^{N}\mathbf{F}_j\cdot\mathbf{p}_j/m_j}{\sum_{k=1}^{N}\mathbf{p}_k^2/m_k}\right]\mathbf{p}_i. \tag{4.35}$$

Equations (4.35) have, by construction, the conserved quantity

$$K=\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i}=\frac{L}{2}kT, \tag{4.36}$$

where L is a constant to be specified.

The non-Hamiltonian equations of motion Eqs. (4.35) have a compressibility determined by the momentum equation given by

$$\kappa=-(dN-1)\frac{\sum_{i=1}^{N}\mathbf{F}_i\cdot\mathbf{p}_i/m_i}{\sum_{k=1}^{N}\mathbf{p}_k^2/m_k}=\frac{\dot{\phi}(dN-1)}{LkT} \tag{4.37}$$

so that the phase space metric becomes

$$\sqrt{g}=e^{-\beta\phi(\mathbf{r})} \tag{4.38}$$

if $L=dN-1$, consistent with Eq. (4.32). In contrast to the previous examples of this section, the complicated dependence of the metric on the coordinates is such that a transformation to incompressible dynamics, if it exists, would likely be highly nontrivial.

If Eq. (4.36) is the only conserved quantity, then by the procedure of Sec. II, the microcanonical partition function generated by the dynamics will be

$$\Omega=\int d^N\mathbf{p}d^N\mathbf{r}e^{-\beta\phi(\mathbf{r})}\delta\left(\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i}-(dN-1)kT\right), \tag{4.39}$$

which is exactly the isokinetic partition function.

Note that, in this case, the use of Eq. (3.1) will generate the important configurational part of the phase space distribution. This can be seen by noting that Eq. (3.1) reduces, for this example, to

$$\frac{d\ln\tilde{f}}{dt} = -\frac{1}{kT}\frac{d}{dt}\phi(\mathbf{r}) \tag{4.40}$$

or

$$\tilde{f} \propto e^{-\phi(\mathbf{r})/kT}. \tag{4.41}$$

The proportionality constant, however, can be any function $f_0(\Sigma_{i=1}^{N}\mathbf{p}_i^2/m_i)$ since this will satisfy $df_0/dt=0$. The choice of f_0 is consistent with Eqs. (4.35) is the δ function appearing in Eq. (4.39). It is clear, however, that apart from the kinetic factor the isokinetic ensemble is a special case in which Eq. (3.1) leads to a correct result.

E. Conclusions: *NVT* dynamics

In practice, several different types of thermostatting schemes are employed in systems with no external forces.

(i) If one Nosé–Hoover chain is used, i.e., global thermostatting, and there are no "hidden" conservation laws or linear dependencies and the system is ergodic, an *NVT* ensemble is produced in the particle positions. The momentum distribution is also correctly reproduced apart from the angular components of the center-of-mass momentum. Provided the Hamiltonian $H(x)$ does not depend on these angular degrees of freedom, which is most often the case, the distribution will nevertheless be correct. With the center of mass initially set to zero ($\mathbf{P}(0)=0$ is a fixed point of the dynamics) an $(N-1)VT$ distribution results as described elsewhere provided $L=d(N-1)$.[40,46] In fact, most calculations are performed using a global thermostat, keeping the center-of-mass fixed.[50]

(ii) If one thermostat chain per molecule type is employed (with the number of molecule types greater than one) then the center-of-mass conservation law is disrupted and, assuming no other hidden conservation laws and ergodic dynamics, a true *NVT* ensemble will be produced.

These two options are used when approximate dynamical information is to be extracted from the simulations (only Newtonian dynamics formally yields proper dynamical information. However, within a set of well defined approximations, NHC dynamics can be used to generate approximate dynamical information given appropriate care and caveats[51]).

Next, it should be noted that the Nosé–Hoover equations, Eqs. (4.3), may not generate a canonical distribution even when an external force is operative. Consider the case of a single harmonic oscillator coupled to a Nosé–Hoover thermostat. It is well known that this system does not generate a canonical distribution in the physical variables.[2,49] However, when the Nosé–Hoover chain method[49] is used, a canonical distribution is obtained. This observation suggests that in the case of the Nosé–Hoover oscillator, there is an additional conservation law that has not been identified. This issue is discussed in more detail in Appendix B.

Similarly, consider a system in which there is weak coupling between the degrees of freedom. Realistic systems that are weakly coupled include proteins, which, for surprisingly long times, can be described with normal coordinates.[52–55] The extreme weak coupling limit is a separable dynamics with dN conservation laws. In this limit, one thermostat chain per degree of freedom is required to generate the *NVT* ensemble (each degree of freedom should be thermalized in-

dependently). This method, called "massive thermostatting", significantly enhances sampling in stiff systems with weak coupling.[48,56,57] Under massive thermostatting, dynamical information is clearly destroyed.

V. THE ISOTHERMAL–ISOBARIC ENSEMBLE

The isothermal–isobaric ensemble is of considerable importance, as it most closely reflects the conditions under which chemical and biochemical experiments are performed. Indeed, if one wishes to calculate the Gibbs free energy in a MD simulation, the isothermal–isobaric ensemble should be employed. The isothermal–isobaric ensemble is characterized by an applied external pressure P_{ext}, temperature T, and particle number N. The ensemble is generated by allowing the volume V to fluctuate. Thus, the volume must be introduced as a dynamical variable in the equations of motion. Volume fluctuations can be treated in a number of different ways. First, there are purely isotropic volume fluctuations, in which the container varies uniformly in all directions. Liquid systems at constant pressure undergo such uniform volume changes. In addition, there are fully flexible cell fluctuations, in which all cell lengths and angles vary independently. The fully flexible case describes the fluctuations of solid/crystalline systems. In the latter case, it is convenient to introduce the full cell matrix, $\overset{\leftrightarrow}{\mathbf{h}}$, whose d columns contain the components of each of the d vectors describing the parallelepiped. The volume V is given by $V=\det(\overset{\leftrightarrow}{\mathbf{h}})$. (Note, liquids do not support shear modes and, hence, cannot be treated in the fully flexible cell ensemble.)

For isotropic volume fluctuations, the partition function is

$$\Delta(N,P_{\text{ext}},T) = \int_0^\infty dV e^{-\beta P_{\text{ext}}V} \int d^N\mathbf{p} \int_{D(V)} d^N\mathbf{r}\, e^{-\beta H(\mathbf{p},\mathbf{r})}. \tag{5.1}$$

A number of non-Hamiltonian molecular dynamics algorithms have been proposed to generate the phase space distributions in Eqs. (5.1). Below, several examples of such algorithms will be analyzed based on the non-Hamiltonian MD procedure of Sec. II and difficulties associated with these schemes discussed.

A. The Hoover algorithm

Consider, first, the dynamical system proposed in Refs. 2 and 3. The equations of motion are

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \frac{p_\epsilon}{W}\mathbf{r}_i, \quad \dot{\mathbf{p}}_i = \mathbf{F}_i - \frac{p_\epsilon}{W}\mathbf{p}_i - \frac{p_\eta}{Q}\mathbf{p}_i, \quad \dot{V} = \frac{dVp_\epsilon}{W},$$

$$\dot{p}_\epsilon = dV(P_{\text{int}}-P_{\text{ext}}) - \frac{p_\eta}{Q}p_\epsilon, \quad \dot{\eta} = \frac{p_\eta}{Q}, \tag{5.2}$$

$$\dot{p}_\eta = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} + \frac{p_\epsilon^2}{W} - LkT.$$

Note that the volume V has been incorporated into the equations of motion. The momentum p_ϵ is not related to dV/dt, itself, but rather to a variable $d\epsilon/dt$, with $\epsilon = (1/d)\ln(V/V_0)$. The parameter V_0 is an arbitrary reference

volume, usually set equal to the initial volume $V(0)$. The variable p_ϵ acts as a "barostat" that is driven by the fluctuations of the internal pressure P_{int} about the applied external pressure P_{ext}. The former is given by

$$P_{int}=\frac{1}{dV}\left[\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i}+\sum_{i=1}^{N}\mathbf{r}_i\cdot\mathbf{F}_i-(dV)\frac{\partial\phi}{\partial V}\right].$$

(5.3)

Note that, in Eqs. (5.2), both the particles and the barostat are coupled to a single Nosé–Hoover thermostat.

Equations (5.2) have the conserved energy

$$H'=H(\mathbf{p},\mathbf{r})+\frac{p_\epsilon^2}{2W}+\frac{p_\eta^2}{2Q}+LkT\eta+P_{ext}V$$

(5.4)

and when $\Sigma_{i=1}^N\mathbf{F}_i=0$, the additional momentum conservation laws

$$\mathbf{P}e^{\epsilon+\eta}=\mathbf{K}.$$

(5.5)

Equation (5.5) implies that the d components of $\mathbf{P}$ are linearly dependent. Moreover, when $\Sigma_i\mathbf{F}_i=0$, the center-of-mass positions $\mathbf{R}$ are driven variables.

The procedure of Sec. II for constructing the microcanonical partition corresponding to Eq. (5.2) will now be applied, assuming $\Sigma_{i=1}^N\mathbf{F}_i\neq0$. The compressibility of Eq. (5.2) is

$$\kappa=\sum_{i=1}^{N}\left[\nabla_{\mathbf{p}_i}\cdot\dot{\mathbf{p}}_i+\nabla_{\mathbf{r}_i}\cdot\dot{\mathbf{r}}_i\right]+\frac{\partial\dot\eta}{\partial\eta}+\frac{\partial\dot{p}_\eta}{\partial p_\eta}+\frac{\partial\dot{V}}{\partial V}+\frac{\partial\dot{p}_\epsilon}{\partial p_\epsilon}$$

$$=\frac{dp_\epsilon}{W}-\frac{(dN+1)p_\eta}{Q}=d\dot\epsilon-(dN+1)\dot\eta$$

(5.6)

and since $d\epsilon=\ln V$, the phase space metric is given by

$$\sqrt{g}=\frac{1}{V}e^{(dN+1)\eta}.$$

(5.7)

Thus, if there are no other conservation laws apart from Eq. (5.4), the microcanonical partition function becomes

$$\Omega_{T,P_{ext}}(N,C_1)=\int dVdp_\epsilon d^N\mathbf{p}d^N\mathbf{r}d\eta dp_\eta\frac{1}{V}e^{(dN+1)\eta}$$

$$\times\delta\left(H(\mathbf{p},\mathbf{r})+\frac{p_\epsilon^2}{2W}+\frac{p_\eta^2}{2Q}+LkT\eta\right.$$

$$\left.+P_{ext}V-C_1\right).$$

(5.8)

Using the δ function to integrate out the variable η, one obtains

$$\Omega_{T,P_{ext}}(N,C_1)=\frac{e^{\beta C_1}}{(dN+1)kT}\int dp_\eta e^{-\beta p_\eta^2/2Q}$$

$$\times\int dp_\epsilon e^{-\beta p_\epsilon^2/2W}\int dV\frac{1}{V}e^{-\beta P_{ext}V}$$

$$\times\int d^N\mathbf{p}\int_{D(V)}d^N\mathbf{r}e^{-\beta H(\mathbf{p},\mathbf{r})},$$

(5.9)

where the parameter L has been taken to be $L=dN+1$.

Due to the presence of the $1/V$ factor in the volume integration, the correct isothermal–isobaric ensemble distribution function is *not* generated as pointed out by Hoover. The difficulty arises from the fact that the non-Hamiltonian equations of motion, Eqs. (5.2), do not have the desired compressibility which, in turn, leads to an incorrect phase space metric and an extra factor of $1/V$.[2,3]

Equations (5.2) become more pathological when $\Sigma_i\mathbf{F}_i=0$, and the additional difficulties caused by the conservation laws given in Eq. (5.5), must be treated. Following the results of the previous section, the partition function becomes

$$\Omega_{T,P_{ext}}(N,C_1,K)=\int dVdp_\epsilon d^{N-1}\mathbf{p}'dP$$

$$\times\int_{D(V)}d^{N-1}\mathbf{r}'d\eta dp_\eta\frac{1}{V^{1-1/d}}$$

$$\times e^{(d(N-1)+2)\eta}$$

$$\times\delta\left(H(\mathbf{p}',P,\mathbf{r}')+\frac{p_\epsilon^2}{2W}+\frac{p_\eta^2}{2Q}+LkT\eta\right.$$

$$\left.+P_{ext}V-C_1\right)\delta(Pe^{\epsilon+\eta}-K).$$

(5.10)

Now, using the δ function $\delta(Pe^{\epsilon+\eta}-K)$ to integrate over the variable η, one obtains

$$\Omega_{T,P_{ext}}(N,C_1,K)=\frac{1}{K}\int dVdp_\epsilon d^{N-1}\mathbf{p}'\,dP$$

$$\times\int_{D(V)}d^{N-1}\mathbf{r}'dp_\eta\frac{1}{V^{N+1/d}}\left(\frac{K}{P}\right)^{d(N-1)+2}$$

$$\times\delta\left(H(\mathbf{p}',P,\mathbf{r}')+\frac{p_\epsilon^2}{2W}+\frac{p_\eta^2}{2Q}\right.$$

$$\left.+LkT\ln\left(\frac{K}{PV^{1/d}}\right)+P_{ext}V-E\right).$$

(5.11)

The partition function can be further simplified using the energy δ function to perform the integration over p_η,

$$\Omega_{T,P_{ext}}(N,C_1,K)=\frac{\sqrt{2Q}}{K}\int dVdp_\epsilon d^{N-1}\mathbf{p}'dPd^{N-1}\mathbf{r}'\frac{1}{V^{N+1/d}}\left(\frac{K}{P}\right)^{d(N-1)+2}$$

$$\times\frac{1}{\sqrt{E-H(\mathbf{p}',P,\mathbf{r}')-(p_\epsilon^2/2W)-LkT\ln[K/(PV^{1/d})]-P_{ext}V}}.$$

(5.12)

Finally, the integration over p_ϵ can be performed via the substitution $p_\epsilon = \sqrt{2W}a \sin\theta$, where $-\pi/2 \leq \theta \leq \pi/2$, and $a^2 = E - H(\mathbf{p}', P, \mathbf{r}') - LkT \ln[K/(PV^{1/d})] - P_{\text{ext}}V$, and one obtains, after integration over the $N-1$ particle positions and momenta,

$$\Omega(N, P_{\text{ext}}, T, E, K)$$

$$\propto \frac{\sqrt{4QW}\pi}{K} \int dV \int dP \, \frac{1}{V^{1+1/d}} \left(\frac{K}{P}\right)^{d(N-1)+2} \qquad (5.13)$$

independent of the potential!

Figure 4 shows the momentum and volume distributions for a free particle in one spatial dimension obtained by integrating Eqs. (5.2). The figure shows that $f(V) \sim 1/V^2$ and $f(p) \sim 1/p^2$, which could be deduced by following the above analysis for this special case. Since the distributions are not normalizable in the range $[0,\infty]$, normalization is performed from on $[V_{\min},\infty]$ or $[P_{\min},\infty]$, where $V_{\min}$ and $P_{\min}$ are the smallest values obtained in the course of the simulation. For N free particles, the correct volume distribution is $f(V)$
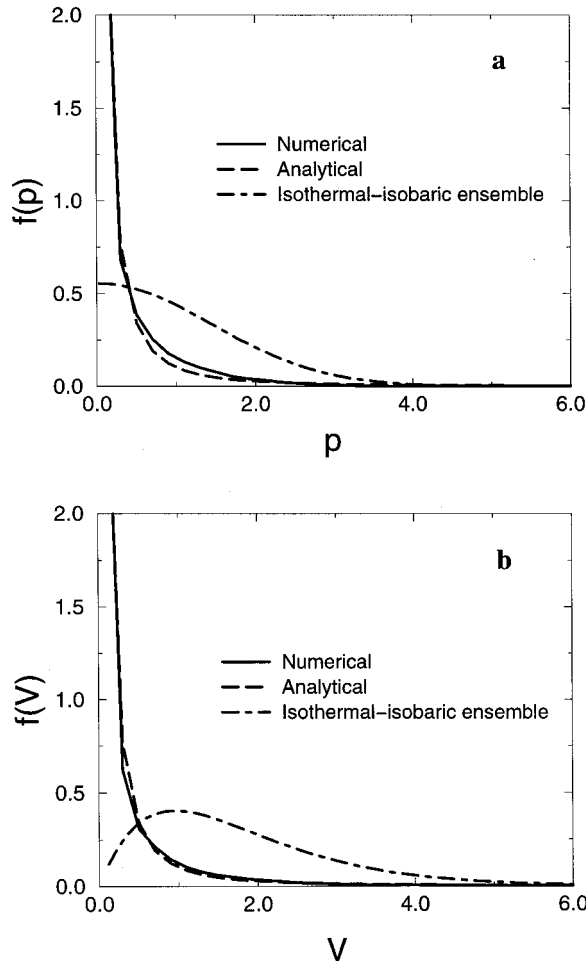

FIG. 4. (a) The momentum distribution function for a one-dimensional free particle using Hoover algorithm (solid line) [$m=1$, $kT=1$, $P_{\text{ext}}=1$, $p(0)=1$, $x(0)=0$, $V(0)=1$, $W=18$, $Q=1$, $p_\eta(0)=1$ with a time step $\Delta t = 0.02$] compared to the analytical (dashed line) and the isothermal-isobaric ensemble (dot dashed line) distribution. (b) The same for the volume distribution function.

$\propto V^N \exp(-P_{\text{ext}}V/kT)$, so that Eqs. (5.2) should generate $f(V) \propto V \exp(-P_{\text{ext}}V/kT)$ for this example which, as Fig. 4(b) shows, is clearly not the case.

The pathology is further underscored by considering two particles in one dimension interacting via a periodic potential of the form

$$\phi(x_1, x_2, V) = \frac{m\omega^2 V^2}{4\pi^2}\left[1 - \cos\left(\frac{2\pi(x_1 - x_2)}{V}\right)\right]. \qquad (5.14)$$

The distributions in the center-of-mass momentum and volume resulting from numerical integration of Eqs. (5.2) are shown in Fig. 5. In agreement with Eq. (5.13), the distributions obtained are of the form, $f(P) \sim 1/P^3$ and $f(V) \sim 1/V^2$, are independent of the potential, and are not those of the NPT ensemble.

The preceding analysis illustrates both the problems associated with an incorrect compressibility and the use of a single global thermostat when there is no net force on the system. As was shown for the case of the NVT ensemble, the latter problem can be solved by coupling a Nosé–Hoover chain thermostat to the system and rewriting Eqs. (5.2) as

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \frac{p_\epsilon}{W}\mathbf{r}_i, \quad \dot{\mathbf{p}}_i = \mathbf{F}_i - \frac{p_\epsilon}{W}\mathbf{p}_i - \frac{p_{\eta_1}}{Q_1}\mathbf{p}_i,$$

$$\dot{V} = \frac{dVp_\epsilon}{W}, \quad \dot{p}_\epsilon = dV(P_{\text{int}} - P_{\text{ext}}) - \frac{p_{\eta_1}}{Q_1}p_\epsilon,$$

$$(5.15)$$

$$\dot{\eta}_k = \frac{p_{\eta_k}}{Q_k}, \quad \dot{p}_{\eta_1} = \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i} + \frac{p_\epsilon^2}{W} - (dN+1)kT - \frac{p_{\eta_2}}{Q_2}p_{\eta_1},$$

$$\dot{p}_{\eta_k} = \frac{p_{\eta_{k-1}}^2}{Q_{k-1}} - kT - \frac{p_{\eta_{k+1}}}{Q_{k+1}}p_{\eta_k}, \quad \dot{p}_{\eta_M} = \frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - kT.$$

After elimination of dependent and driven variables, the equations of motion become

$$\dot{\mathbf{r}}_i' = \frac{\mathbf{p}_i'}{m_i'} + \frac{p_\epsilon}{W}\mathbf{r}_i', \quad \dot{\mathbf{p}}_i' = \mathbf{F}_i' - \frac{p_\epsilon}{W}\mathbf{p}_i' - \frac{p_{\eta_1}}{Q_1}\mathbf{p}_i',$$

$$\dot{P} = -\frac{p_\epsilon}{W}P - \frac{p_{\eta_1}}{Q_1}P, \quad \dot{V} = \frac{dVp_\epsilon}{W},$$

$$\dot{p}_\epsilon = dV(P_{\text{int}} - P_{\text{ext}}) - \frac{p_{\eta_1}}{Q_1}p_\epsilon, \quad \dot{\eta}_1 = \frac{p_{\eta_1}}{Q_1},$$

$$\dot{\eta}_c = \sum_{k=2}^{M}\frac{p_{\eta_k}}{Q_k}, \qquad (5.16)$$

$$\dot{p}_{\eta_1} = \sum_{i=1}^{N-1}\frac{\mathbf{p}_i^2}{m_i} + \frac{P^2}{M} + \frac{p_\epsilon^2}{W} - (dN+1)kT - \frac{p_{\eta_2}}{Q_2}p_{\eta_1},$$

$$\dot{p}_{\eta_k} = \frac{p_{\eta_{k-1}}^2}{Q_{k-1}} - kT - \frac{p_{\eta_{k+1}}}{Q_{k+1}}p_{\eta_k},$$

$$\dot{p}_{\eta_M} = \frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - kT,$$
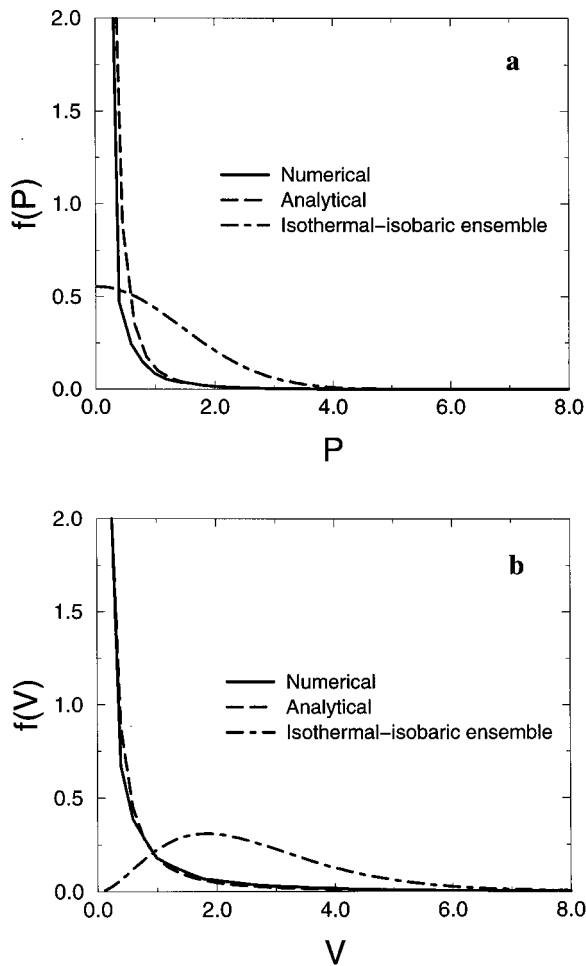
and the phase space metric is given by

FIG. 5. (a) The center-of-mass momentum distribution function for two one-dimensional particles interacting via a periodic potential with $m=1$, $\omega=1$ (see text) using the Hoover algorithm (solid line) [$m_1=m_2=1$, $kT=1$, $P_{ext}=1$, $p_1(0)=p_2(0)=1$, $x_1(0)=0$, $x_2(0)=0.5$, $V(0)=1$, $W=27$, $Q=2$, $p_\eta(0)=\sqrt{2}$, $\Delta t=0.02$] compared to the analytical (dashed line) and the isothermal–isobaric ensemble (dot dashed line) distribution. (b) The same for the volume distribution function.

$$\sqrt{g}=\frac{1}{V^{1-1/d}}e^{(d(N-1)+2)\eta_1+\eta_c} \tag{5.17}$$

and, by the reasoning of Sec. IV, the microcanonical partition function obtained after integration over the variables η_1 and η_c is

$$\Omega \propto \int dVe^{-\beta P_{ext}V}\int d^{N-1}\mathbf{p}'\,dP\left(\frac{P}{K}\right)^{d-1}$$
$$\times \int_{D(V)} d^{N-1}\mathbf{r}'e^{-\beta H(\mathbf{p}',\mathbf{r}',P)}, \tag{5.18}$$

where, again, P and $\mathbf{p}'$ denote center-of-mass ($P=|\mathbf{P}|$) and relative momenta, respectively.

Equation (5.18) is not a correct isothermal–isobaric ensemble partition function (NPT), again because of the $1/V$ factor in the volume integration. This can be seen by writing Eq. (5.18) in the form,

$$\Omega \propto \int dVe^{-\beta P_{ext}V}\frac{1}{V}\int d^{N-1}\mathbf{p}'\,dP\left(\frac{P}{K}\right)^{d-1}$$
$$\times \int_{D(V)} d^{N-1}\mathbf{r}'\,d\mathbf{R}e^{-\beta H(\mathbf{p}',\mathbf{r}',P)}, \tag{5.19}$$

where unity has been introduced in the form of $(1/V)\int d\mathbf{R}$. Thus, even if the Hamiltonian does not depend on the center-of-mass positions and angular components of the center-of-mass momentum, Eq. (5.18) still does not represent a correct isothermal–isobaric distribution function. However, Eq. (5.18) is a proper $(N-1)PT$ distribution. Note that if the choice $\mathbf{K}=0$ is made, then the center-of-mass momenta do not evolve. Then, the equation for P must be eliminated in Eqs. (5.16) so that the metric factor reduces to $\sqrt{g}=(1/V)\exp(dN\eta_1+\eta_c)$. In this case, the Hoover algorithm will generate

$$\Omega \propto \int dVe^{-\beta P_{ext}V}\frac{1}{V}\int d^{N-1}\mathbf{p}'\int_{D(V)} d^{N-1}\mathbf{r}'e^{-\beta H(\mathbf{p}',\mathbf{r}')}, \tag{5.20}$$

which is not an $(N-1)PT$ ensemble due to the presence of the $1/V$ factor in the volume integration.

As an illustration of Eq. (5.18), the two-particle system subject to the potential of Eq. (5.14) was integrated using the Hoover algorithm with a chain thermostat of length of three. The center-of-mass momentum and volume distributions are shown in Fig. 6. The center-of-mass momentum distribution is, for $P>0$, given by

$$f(P)=\sqrt{\frac{\beta}{m\pi}}e^{-\beta P^2/4m} \tag{5.21}$$

($m=1$ and $\beta=1$ in this example) while the volume distribution $f(V)$ can only be obtained by numerical integration over position due to the form of the potential. The correct NPT volume distribution is then given by

$$f(V)=\frac{V^2e^{-\beta P_{ext}V}\int dxe^{-\beta\tilde{\phi}(x,V)}}{\int dVV^2e^{-\beta P_{ext}V}\int dxe^{-\beta\tilde{\phi}(x,V)}}, \tag{5.22}$$

whereas the Hoover algorithm generates

$$f(V)=\frac{Ve^{-\beta P_{ext}V}\int dxe^{-\beta\tilde{\phi}(x,V)}}{\int dVVe^{-\beta P_{ext}V}\int dxe^{-\beta\tilde{\phi}(x,V)}}, \tag{5.23}$$

where, in both expressions, $\tilde{\phi}(x,V)=\phi(x,0,V)$ with $\phi(x,y,V)$ defined in Eq. (5.14). While the correct center-of-mass momentum distribution is reproduced for $P>0$, the volume distribution is different by a factor equal to the expected factor of $1/V$ [correct if $(N-1)PT$ is desired and incorrect if NPT is desired].

B. The Melchionna–Ciccotti–Holian algorithm

In an effort to correct for some of the deficiencies of the original Hoover formulation, Melchionna, Ciccotti, and Holian (MCH)[41] have suggested that Hoover's equations be modified according to
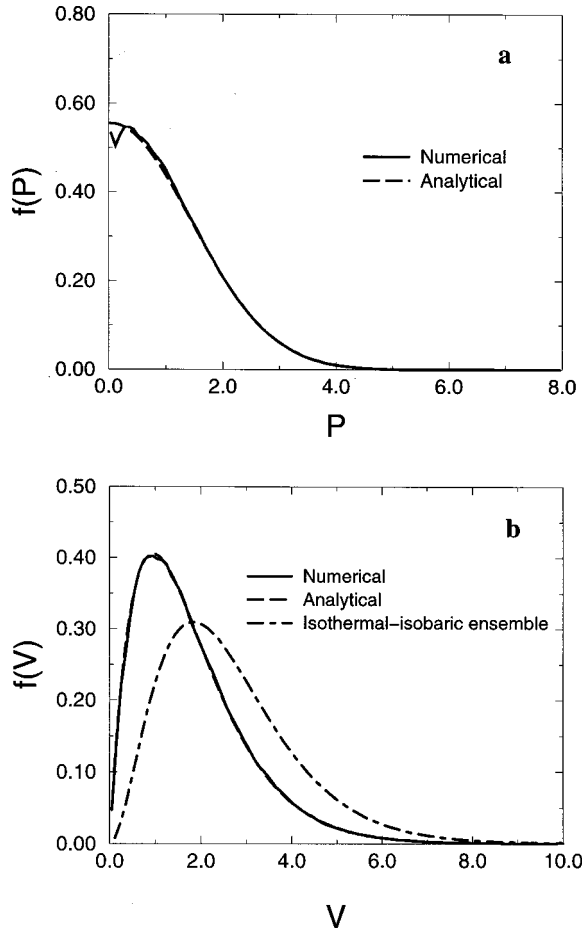
FIG. 6. (a) The center-of-mass momentum distribution function for two one-dimensional particles interacting via a periodic potential with $m=1$, $\omega=1$ (see text) using the Hoover algorithm with a chain thermostat of $M=3$ (solid line) $[m_1=m_2=1, kT=1, P_{ext}=1, p_1(0)=p_2(0)=1, x_1(0)=0, x_2(0)=0.5, V(0)=1, W=27, Q_1=2, Q_2=Q_3=1, p_{\eta_i}(0)=(-1)^{i-1}\sqrt{Q_i}]$ compared to the analytical distribution (dashed line). In this case, the analytically predicted distribution is identical to the isothermal–isobaric canonical ensemble distribution. (b) The volume distribution function (solid line) compared to the analytical (dashed line) and the isothermal-isobaric ensemble (dot dashed line) distribution.

$$\dot{\mathbf{r}}_i=\frac{\mathbf{p}_i}{m_i}+(\mathbf{r}_i-\mathbf{R})\frac{p_\epsilon}{W}, \quad \dot{\mathbf{p}}_i=\mathbf{F}_i-\frac{p_\epsilon}{W}\mathbf{p}_i-\frac{p_\eta}{Q}\mathbf{p}_i,$$

$$\dot{V}=\frac{dVp_\epsilon}{W}, \quad \dot{p}_\epsilon=dV(P_{int}-P_{ext})-\frac{p_\eta}{Q}p_\epsilon, \quad (5.24)$$

$$\dot{\eta}=\frac{p_\eta}{Q}, \quad \dot{p}_\eta=\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i}+\frac{p_\epsilon^2}{W}-(dN+1)kT,$$

where $\mathbf{R}$ is the position of the center-of-mass of the system. [Note that Eqs. (5.24) contain a slight modification of the original equations of motion presented in Ref. 41, namely that the variable p_ϵ is coupled to the thermostat. This modification only serves to ensure that the distribution of p_ϵ is of a Gaussian form.] The internal pressure associated with Eqs. (5.24) is

$$P_{int}=\frac{1}{dV}\left[\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i}+\sum_{i=1}^{N}(\mathbf{r}_i-\mathbf{R})\cdot\mathbf{F}_i-(dV)\frac{\partial\phi}{\partial V}\right]. \quad (5.25)$$

As formulated,[41] the MCH equations have the same conserved energy given in Eq. (5.4) and have a metric of the form

$$\sqrt{g}=e^{(dN+1)\eta} \quad (5.26)$$

and will, therefore, generate a correct NPT ensemble if $\Sigma_i\mathbf{F}_i\neq 0$.

When $\Sigma_i\mathbf{F}_i=0$ and the single global thermostat is used, the MCH equations of motion have the same pathology as the Hoover equations, i.e., a distribution that is independent of the potential [cf Eq. (5.13)]. One might consider remedying this problem by coupling the equations of motion to a Nosé–Hoover chain thermostat,

$$\dot{\mathbf{r}}_i=\frac{\mathbf{p}_i}{m_i}+(\mathbf{r}_i-\mathbf{R})\frac{p_\epsilon}{W}, \quad \dot{\mathbf{p}}_i=\mathbf{F}_i-\frac{p_\epsilon}{W}\mathbf{p}_i-\frac{p_{\eta_1}}{Q_1}\mathbf{p}_i,$$

$$\dot{V}=\frac{dVp_\epsilon}{W}, \quad \dot{p}_\epsilon=dV(P_{int}-P_{ext})-\frac{p_{\eta_1}}{Q_1}p_\epsilon,$$

$$\dot{\eta}_k=\frac{p_{\eta_k}}{Q_k}, \quad \dot{p}_{\eta_1}=\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i}+\frac{p_\epsilon^2}{W}-(dN+1)kT-\frac{p_{\eta_2}}{Q_2}p_{\eta_1},$$

$$(5.27)$$

$$\dot{p}_{\eta_k}=\frac{p_{\eta_{k-1}}^2}{Q_{k-1}}-kT-\frac{p_{\eta_{k+1}}}{Q_{k+1}}p_{\eta_k},$$

$$\dot{p}_{\eta_M}=\frac{p_{\eta_{M-1}}^2}{Q_{M-1}}-kT.$$

Equations (5.27) have the conserved energy

$$H'=H(\mathbf{p},\mathbf{r})+\frac{p_\epsilon^2}{2W}+\sum_{k=1}^{M}\frac{p_{\eta_k}^2}{2Q_k}+(dN+1)kT\eta_1+kT\eta_c$$

$$+P_{ext}V, \quad (5.28)$$

and, when $\Sigma_i\mathbf{F}_i=0$, the same momentum conservation laws as Eq. (5.5).

It has been pointed out in Ref. 5 that Eqs. (5.24) cannot, in general, generate an NPT isothermal–isobaric ensemble. Apart from the pathology associated with the momentum conservation condition, Eq. (5.5), which was not addressed in Ref. 41 since the authors relied solely on the Liouville equation as was done in Ref. 40, there are additional difficulties involving the coupling of center-of-mass momenta to the dynamics that must be addressed.

The pathology associated with Eqs. (5.27) can be seen by computing from the equation for $\dot{\mathbf{r}}_i$ an equation for $\mathbf{R}$, the center-of-mass position

$$\dot{\mathbf{R}}=\frac{\mathbf{P}}{M}, \quad (5.29)$$

where $\mathbf{P}$ is the center-of-mass momentum, and M the total mass of the system. In addition, it is clear that, if $\Sigma_{i=1}^{N}\mathbf{F}_i=0$, the conserved energy does not depend on $\mathbf{R}$ nor are the $\mathbf{R}$ coupled to the barostat p_ϵ. In fact, the internal pressure, which can be expressed as

$$\tilde{P}_{int}=P_{int}+\mathbf{R}\cdot\sum_{i=1}^{N}\mathbf{F}_i=P_{int} \quad (5.30)$$

does not depend explicitly on the center-of-mass in this limit. Thus, **R** has become an auxiliary variable and does not contribute to the phase space.

When the center-of-mass is eliminated and $d-1$ components of the center of mass momentum are eliminated, the equations of motion become identical to Eqs. (5.16), the metric becomes

$$\sqrt{g} = \frac{1}{V^{1-1/d}} e^{[d(N-1)+2]\eta_1 + \eta_c} \qquad (5.31)$$

and, by the reasoning of the last section, Eqs. (5.27) will generate an $(N-1)PT$ ensemble. Again, if the choice **K**=0 is made, then the center-of-mass momentum and the center-of-mass position are both fixed. This is tantamount to completely eliminating the physical translational degrees of freedom of the system, so that the MCH algorithm will, in this case, generate Eq. (5.20).

In order to illustrate the pathology of the MCH algorithm, the same two-particle system subject to the potential of Eq. (5.14) was integrated numerically using Eqs. (5.24) coupled to a Nosé–Hoover chain of length $M=3$. The resulting center-of-mass momentum and volume distributions are shown in Fig. 7. Again, it can be seen that the center-of-mass momentum distribution is correctly generated for $P>0$, but the volume distribution is not. In analogy to the Hoover algorithm, the volume distribution contains a factor of $1/V$ because an $(N-1)PT$ distribution is generated. More details concerning this pathology are given in Appendix C.

C. The Martyna–Tobias–Klein algorithm

The analysis presented in Sec. 5.2 shows that Eqs. (5.24) can only generate the $(N-1)PT$ ensemble when $\Sigma_i \mathbf{F}_i = 0$. These problems have been addressed and corrected by Martyna *et al.*[5] Therefore, we will examine the algorithm presented in Ref. 5 in some detail. Consider the equations of motion proposed by Martyna *et al.*,

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \frac{p_\epsilon}{W} \mathbf{r}_i,$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \left(1 + \frac{1}{N}\right) \frac{p_\epsilon}{W} \mathbf{p}_i - \frac{p_{\eta_1}}{Q_1} \mathbf{p}_i,$$

$$\dot{V} = \frac{dVp_\epsilon}{W},$$

$$\dot{p}_\epsilon = dV(P_{\text{int}} - P_{\text{ext}}) + \frac{1}{N} \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} - \frac{p_{\xi_1}}{Q'} p_\epsilon,$$

$$\dot{\eta}_k = \frac{p_{\eta_k}}{Q_k},$$

$$\dot{p}_{\eta_1} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} - dNkT - \frac{p_{\eta_2}}{Q_2} p_{\eta_1},$$

$$\dot{p}_{\eta_k} = \frac{p_{\eta_{k-1}}^2}{Q_{k-1}} - kT - \frac{p_{\eta_{k+1}}}{Q_{k+1}} p_{\eta_k},$$
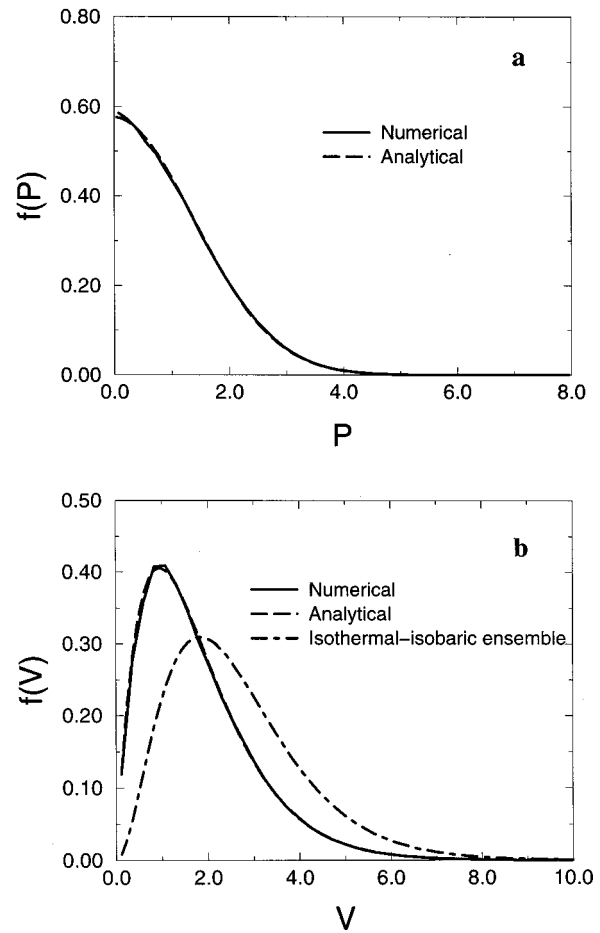
$$(5.32)$$

FIG. 7. (a) The center-of-mass momentum distribution function for two one-dimensional particles interacting via a periodic potential with $m=1$, $\omega=1$ (see text) using the Melchionna–Ciccotti–Holian algorithm with a chain thermostat of $M=3$ (solid line) (with the same initial conditions as in Fig. 6) compared to the analytical distribution (dashed line). In this case, the analytically predicted distribution is identical to the isothermal–isobaric canonical ensemble distribution. (b) The volume distribution function (solid line) compared to the analytical (dashed line) and the isothermal–isobaric ensemble (dot dashed line) distribution.

$$\dot{p}_{\eta_M} = \frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - kT,$$

$$\dot{\xi}_k = \frac{p_{\xi_k}}{Q'_k},$$

$$\dot{p}_{\xi_1} = \frac{p_\epsilon^2}{W} - kT - \frac{p_{\xi_2}}{Q'_2} p_{\xi_1},$$

$$\dot{p}_{\xi_k} = \frac{p_{\xi_{k-1}}^2}{Q'_{k-1}} - kT - \frac{p_{\xi_{k+1}}}{Q'_{k+1}} p_{\xi_k},$$

$$\dot{p}_{\xi_M} = \frac{p_{\xi_{M-1}}^2}{Q'_{M-1}} - kT,$$

which includes a coupling to a Nosé–Hoover chain. In Eqs. (5.34), the internal pressure is given by

$$P_{\text{int}} = \frac{1}{dV}\left[\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i} + \sum_{i=1}^{N}\mathbf{r}_i\cdot\mathbf{F}_i - (dV)\frac{\partial\phi}{\partial V}\right]. \tag{5.33}$$

Note that the particles and barostat are coupled to separate Nosé–Hoover chain thermostats. These equations should be used in practice, as the time scales associated with these degrees of freedom are considerably different. In the remainder of this section, however, the analysis will be simplified by coupling the particles and barostat to the *same* Nosé–Hoover chain thermostat. That is, equations of motion of the form:

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \frac{p_\epsilon}{W}\mathbf{r}_i,$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \left(1+\frac{1}{N}\right)\frac{p_\epsilon}{W}\mathbf{p}_i - \frac{p_{\eta_1}}{Q_1}\mathbf{p}_i,$$

$$\dot{V} = \frac{dVp_\epsilon}{W},$$

$$\dot{p}_\epsilon = dV(P_{\text{int}}-P_{\text{ext}}) + \frac{1}{N}\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i} - \frac{p_{\eta_1}}{Q_1}p_\epsilon,$$

$$\dot{\eta}_k = \frac{p_{\eta_k}}{Q_k}, \tag{5.34}$$

$$\dot{p}_{\eta_1} = \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i} + \frac{p_\epsilon^2}{W} - (dN+1)kT - \frac{p_{\eta_2}}{Q_2}p_{\eta_1},$$

$$\dot{p}_{\eta_k} = \frac{p_{\eta_{k-1}}^2}{Q_{k-1}} - kT - \frac{p_{\eta_{k+1}}}{Q_{k+1}}p_{\eta_k},$$

$$\dot{p}_{\eta_M} = \frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - kT,$$

will be considered.

In the analysis that follows, we will first analyze the equations of motion using $\sum_{i=1}^{N}\mathbf{F}_i\neq 0$, and then consider $\sum_{i=1}^{N}\mathbf{F}_i = 0$. It will be demonstrated that a NPT ensemble is obtained in either case.

The compressibility associated with Eqs. (5.34) is

$$\nabla\cdot\dot{x} = -(dN+1)\frac{p_{\eta_1}}{Q_1} - \sum_{k=2}^{M}\frac{p_{\eta_k}}{Q_k}, \tag{5.35}$$

so that the phase space metric is $\sqrt{g} = \exp[(dN+1)\eta_1+\eta_c]$. Since we are considering the case where $\sum_{i=1}^{N}\mathbf{F}_i\neq 0$, we will assume that there is only one conserved quantity given by

$$H' = H(\mathbf{p},\mathbf{r}) + \frac{p_\epsilon^2}{2W} + \sum_{k=1}^{M}\frac{p_{\eta_k}^2}{2Q_k} + (dN+1)kT\eta_1 + kT\eta_c$$

$$+ P_{\text{ext}}V. \tag{5.36}$$

Applying the non-Hamiltonian procedure, the microcanonical partition function is given by

$$\Omega_{T,P_{\text{ext}}}(N,C_1) = \int dV\int d^N\mathbf{p}d^N\mathbf{r}d^M p_\eta d\eta_1\, d\eta_c\, dp_\epsilon$$

$$\times\exp[(dN+1)\eta_1+\eta_c]\delta(H'-C_1). \tag{5.37}$$

The integration over the variable η_1 using the δ function requires

$$\eta_1 = \frac{1}{(dN+1)kT}\left(E - H(\mathbf{p},\mathbf{r}) - \sum_{k=1}^{M}\frac{p_{\eta_k}^2}{2Q_k} - kT\eta_c - \frac{p_\epsilon^2}{2W}\right.$$

$$\left. - P_{\text{ext}}V\right). \tag{5.38}$$

Substitution of Eq. (5.38) into Eq. (5.37) yields the partition function expression:

$$\Omega(N,P_{\text{ext}},E,T) \propto \int d^M p_\eta e^{-\beta p_\eta^2/2Q}\int dp_\epsilon e^{-\beta p_\epsilon^2/2W}$$

$$\times\int dVe^{-\beta P_{\text{ext}}V}\int d^N\mathbf{p}\int_{D(V)}d^N\mathbf{r}e^{-\beta H(\mathbf{p},\mathbf{r})}$$

$$\propto \Delta(N,P_{\text{ext}},T), \tag{5.39}$$

which demonstrates that the non-Hamiltonian equations (5.34) correctly reproduce the isotropic NPT ensemble distribution function.

When $\sum_{i=1}^{N}\mathbf{F}_i = 0$, there are d additional conservation laws,

$$\mathbf{K} = \mathbf{P}\exp\left[\left(1+\frac{1}{N}\right)\epsilon+\eta_1\right]. \tag{5.40}$$

Again, there are linear dependencies among the components of $\mathbf{P}$ so that $d-1$ components of the center-of-mass momentum must be eliminated. In addition, the center-of-mass position $\mathbf{R}$ is driven by variables and must be eliminated as well. Thus, transforming to a set of coordinates $\{\mathbf{r}',\mathbf{R},\mathbf{p}',\mathbf{P}\}$, which contain the center-of-mass position and momentum, respectively, and eliminating the driven and dependent variables, the equations of motion can be written as

$$\dot{\mathbf{r}}_i' = \frac{\mathbf{p}_i'}{m_i'} + \frac{p_\epsilon}{W}\mathbf{r}_i',$$

$$\dot{\mathbf{p}}_i' = \mathbf{F}_i' - \left(1+\frac{1}{N}\right)\frac{p_\epsilon}{W}\mathbf{p}_i' - \frac{p_{\eta_1}}{Q}\mathbf{p}_i',$$

$$\dot{P} = -\left(1+\frac{1}{N}\right)\frac{p_\epsilon}{W}P - \frac{p_{\eta_1}}{Q}P,$$

$$\dot{V} = \frac{dVp_\epsilon}{W},$$

$$\dot{p}_\epsilon = dV(P_{\text{int}}-P_{\text{ext}}) + \frac{1}{N}\sum_{i=1}^{N-1}\frac{(\mathbf{p}_i')^2}{m_i'} + \frac{1}{N}\frac{P^2}{M} - \frac{p_{\eta_1}}{Q}p_\epsilon,$$

$$\tag{5.41}$$

$$\dot{\eta}_k = \frac{p_{\eta_k}}{Q_k},$$

$$\dot{p}_{\eta_1} = \sum_{i=1}^{N-1} \frac{(\mathbf{p}_i')^2}{m_i'} + \frac{P^2}{M} + \frac{p_\epsilon^2}{W} - LkT - \frac{p_{\eta_2}}{Q_2} p_{\eta_1},$$

$$\dot{p}_{\eta_k} = \frac{p_{\eta_{k-1}}^2}{Q_{k-1}} - kT - \frac{p_{\eta_{k+1}}}{Q_{k+1}} p_{\eta_k},$$

$$\dot{p}_{\eta_M} = \frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - kT,$$

where the parameter L will be determined. The phase space metric for these equations of motion can be shown to be

$$\sqrt{g} = \frac{1}{V^{[VN - 1/d - 1/dN]}} \exp[(dN - d + 2)\eta_1 + \eta_c]. \quad (5.42)$$

Thus, the microcanonical partition function corresponding to Eq. (5.41) is

$$\Omega_{T,P_{\text{ext}}}(N, C_1, C_2) = \int dV \int dP \int d^{N-1}\mathbf{p}' \int_{D(V)} d^{N-1}\mathbf{r}' \int d\eta_1 \, d\eta_c \, d^M p_\eta \, dp_\epsilon$$

$$\times \frac{1}{V^{(1/N) - (1/d) - (1/dN)}} \exp[(dN - d + 2)\eta_1 + \eta_c]$$

$$\times \delta\left(H(\mathbf{p}', P, \mathbf{r}') + \frac{p_\epsilon^2}{2W} + \sum_{k=1}^{M} \frac{p_{\eta_k}^2}{2Q} + LkT_{\eta_1} + kT_{\eta_c} + P_{\text{ext}}V - C_1 \right) \delta\left(P \exp\left[\left(1 + \frac{1}{N} \right) \epsilon + \eta_1 \right] - C_2 \right),$$

$$(5.43)$$

Performing the integration over η_1 using the momentum delta function and remembering that $\epsilon = (1/d)\ln(V)$, gives

$$\Omega_{T,P_{\text{ext}}}(N, C_1, C_2) = \int dV \int dP \int d^{N-1}\mathbf{p}' \int_{D(V)} d^{N-1}\mathbf{r}' \int d\eta_c d^M p_\eta dp_\epsilon \frac{1}{V^{(1/N) - (1/d) - (1/dN)}}$$

$$\times \exp(\eta_c) \left[\frac{C_2}{PV^{1/d[1 + (1/N)]}} \right]^{dN - d + 2} \delta\left(H(\mathbf{p}', P, \mathbf{r}') + \frac{p_\epsilon^2}{2W} + \sum_{k=1}^{M} \frac{p_{\eta_k}^2}{2Q} + LkT \ln\left(\frac{C_2}{PV^{1/d[1 + (1/N)]}} \right) + kT_{\eta_c} \right.$$

$$\left. + P_{\text{ext}}V - C_1 \right).$$

$$(5.44)$$

Finally, integrating over η_c and identifying the parameter L as $dN + 1$, the partition function becomes

$$\Omega_{T,P_{\text{ext}}}(N, C_1, C_2) \propto \int dV \int d^{N-1}\mathbf{p}' \, dP$$

$$\times \int_{D(v)} d^{N-1}\mathbf{r}' P^{d-1} V$$

$$\times \exp(-\beta P_{\text{ext}}V)$$

$$\times \exp(-\beta H(\mathbf{p}', P, \mathbf{r}')). \quad (5.45)$$

Equation (5.45) properly yields the NPT partition function, as can be seen more explicitly by writing $V = \int_{D(V)} d\mathbf{R}$ so that

$$\Omega_{T,P_{\text{ext}}}(N, C_1, C_2) \propto \int dV \int d^{N-1}\mathbf{p}' \, dP \int_{D(V)} d^{N-1}\mathbf{r}'$$

$$\times \int_{D(V)} d\mathbf{R} P^{d-1} \exp(-\beta P_{\text{ext}}V)$$

$$\times \exp(-\beta H(\mathbf{p}', P, \mathbf{r}')). \quad (5.46)$$

Thus, the Martyna–Tobias–Klein (MTK) algorithm will generate a correct isothermal–isobaric ensemble even for the difficult case $\Sigma_i \mathbf{F}_i = 0$. Moreover, if the choice $\mathbf{K} = 0$ is made, then it becomes clear that the Martyna–Tobas–Klein algorithm will correctly generate an $(N-1)PT$ ensemble.

In order to illustrate the performance of the Martyna–Tobias–Klein algorithm, consider the example of a two-particle system subject to the potential of Eq. (5.14). The center-of-mass momentum and volume distributions are shown in Fig. 8. Here, it can be seen that when a global chain thermostat is used, the center-of-mass momentum distribution is correctly generated for $P > 0$ and the volume distribution is also correct. When massive thermostatting is used, the *full* center-of-mass momentum distribution is now properly generated as well as the volume distribution.

It is important to note that, even within the MTK scheme, some aspects of free-particle systems remain pathological. In order to illustrate this, the case of two free particles is considered once again. Figures 9(a) and 9(b) show the center-of-mass momentum and volume distributions obtained when a global chain thermostat is used. It can be seen that the center-of-mass momentum distribution is not correctly generated because of the conservation law Eq. (4.30) on the relative momentum. However, the volume distribution is the correct $f(V) \propto V^2 \exp(-P_{\text{ext}}V/kT)$.

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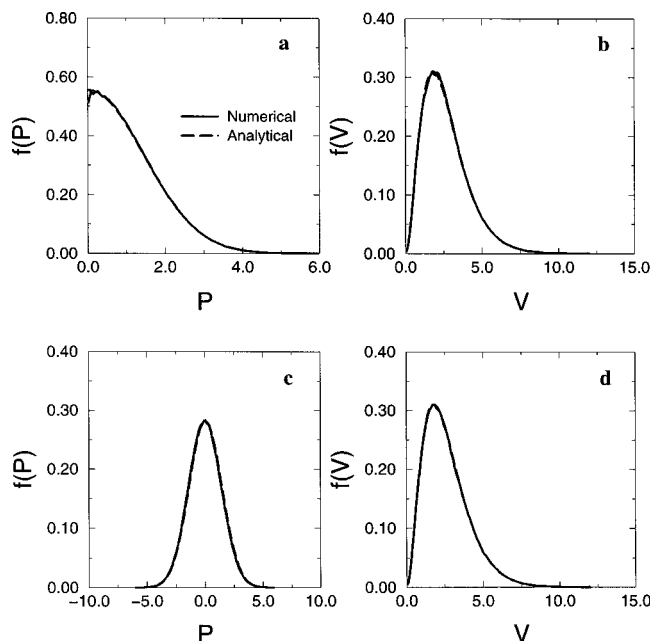Non-Hamiltonian molecular dynamics   1697

FIG. 8. (a) The center-of-mass momentum distribution function for two one-dimensional particles interacting via a periodic potential with $m=1$, $\omega=1$ (see text) using the Martyna–Tobias–Klein global chain thermostat of $M=3$ [with the same initial conditions as in (a)–(b)] (solid line) compared to the analytical distribution (dashed line). (b) The same for the volume distribution function using a global chain thermostat. (c) The same for the center-of-mass momentum distribution function using a massive chain thermostat of $M=3$ for each degree of freedom [with the same initial conditions as in (c)–(d)]. (d) The same for the volume distribution function with a massive chain thermostat. In all cases, the analytically predicted distribution is identical to the isothermal–isobaric canonical ensemble distribution.
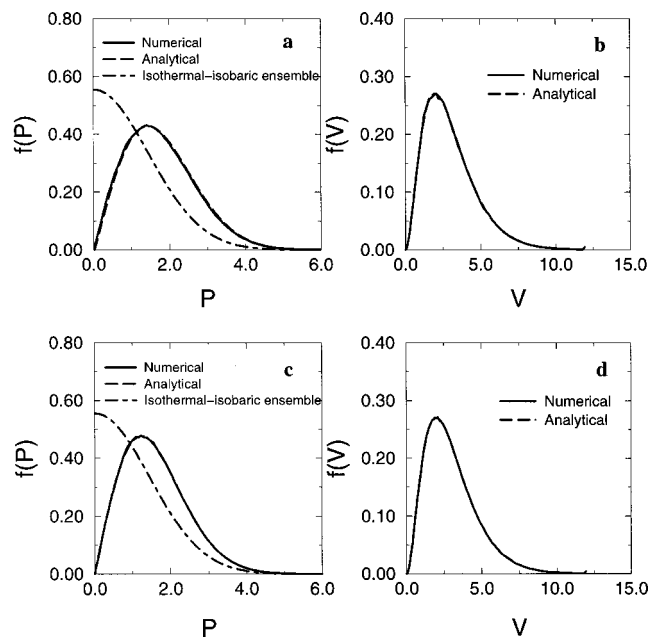

FIG. 9. (a) The center-of-mass momentum distribution function for two one-dimensional free particles using a Martyna–Tobias–Klein global chain of length $M=3$ (solid line) [$\Delta t=0.02$, $m_1=m_2=1$, $kT=1$, $P_{ext}=1$, $p_1(0)=0.8$, $p_2(0)=1.166$, $x_1(0)=0$, $x_2(0)=0.5$, $V(0)=1$, $W=27$, $Q_1=2$, $Q_2=Q_3=1$ for the particle thermostats and $Q_1'=Q_2'=Q_3'=1$ for the barostat thermostats, and all initial thermostat momenta sampled randomly from a Maxwell–Boltzmann distribution] compared to the analytical (dashed line) and the isothermal–isobaric ensemble (dot dashed line) distribution. (b) The volume distribution with a global thermostat (solid line) compared to the analytical distribution (dashed line), which is identical to the isothermal–isobaric canonical ensemble distribution function. (c) The center-of-mass momentum distribution function using a massive chain thermostat of $M=3$ [$m_1=m_2=1$, $kT=1$, $P_{ext}=1$, $p_1(0)=1$, $p_2(0)=1$, $x_1(0)=0$, $x_2(0)=0.5$, $Q_1=Q_2=Q_3=1$ and $p_{\eta_i}(0)=(-1)^{i-1}\sqrt{Q_i}$ for each degree of freedom]. (d) The same for the volume distribution function with a massive thermostat.

Figures 9(c) and 9(d) show the same distributions when each particle is coupled to a separate chain thermostat and the barostat is coupled to a third thermostat. It can be seen that, for free particles, the use of such "massive" thermostatting techniques (one thermostat chain on each particle and one on the barostat) cannot give the correct center-of-mass momentum distribution. Although under massive thermostatting, the momentum conservation law Eq. (5.40) is no longer valid, the two momenta must be treated as independent Gaussian random variables restricted to the range $[0,\infty]$. In this case, the distribution of $P=p_1+p_2$ is the convolution $f(p_1)*f(p_2)$. Although $f(p_1)$ and $f(p_2)$ are Gaussian distributions, the convolution of these two functions, subject to the restriction that p_1 and p_2 are positive, is *not* a Gaussian in p_1+p_2. The same result would be expected in the *NVT* ensemble as well. Nonetheless, as Fig. 9(c) shows, the volume distribution is correctly generated.

D. Conclusions: *NPT*

In this subsection, the results of the various *NPT* algorithms are summarized:

(i) The Hoover algorithm cannot generate an *NPT* ensemble distribution as Hoover recognized. When $\Sigma_{i=1}^N \mathbf{F}_i \neq 0$, the volume distribution will be incorrect by a factor of $1/V$ with or without the use of chain thermostatting. When $\Sigma_{i=1}^N \mathbf{F}_i = 0$, serious pathologies result if a single Nosé–Hoover thermostat is used. The volume distribution is $f(V)$

$\sim 1/V^{1+1/d}$ and the center of mass momentum distribution is $f(P) \sim 1/P^{d(N-1)+2}$, independent of potential. If a chain thermostat is employed, the center of mass momentum distribution is correct but the volume distribution contains a factor of $1/V$, indicating that an $(N-1)PT$ ensemble is generated. If the choice $\mathbf{K}=0$ is made, the Hoover algorithm will generate Eq. (5.20) which has an undesirable factor of $1/V$ weighting the phase space.

(ii) The Melchionna–Ciccotti–Holian algorithm is capable of generating a proper *NPT* ensemble distribution if $\Sigma \mathbf{F}_i \neq 0$. If $\Sigma \mathbf{F}_i = 0$, the most common case, an $(N-1)PT$ ensemble is generated provided the center-of-mass is permitted to evolve and chain thermostats are employed. With $\Sigma \mathbf{F}_i = 0$, the Melchionna–Ciccotti–Holian can never generate an *NPT* ensemble (see Appendix C). Finally, if the choice $\mathbf{K}=0$ is made, the Melchionna–Ciccotti–Holian algorithm will generate Eq. (5.20).

(iii) The Martyna–Tobias–Klein algorithm generates the correct momentum and configuration space distributions as well as the volume distribution of the *NPT* ensemble. Moreover, if the choice $\mathbf{K}=0$ is made, then the Martyna–Tobias–Klein algorithm will generate an $(N-1)PT$ ensemble as expected.

VI. SYSTEMS SUBJECT TO HOLONOMIC CONSTRAINTS

In this section, a set of non-Hamiltonian equations of motion for a system subject to a single holonomic constraint will be considered and the corresponding phase space metric derived.[23–28] Consider an N-particle system with Cartesian positions $\mathbf{r} = \{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ and Cartesian momenta $\mathbf{p} = \{\mathbf{p}_1, \dots, \mathbf{p}_N\}$ subject to a holonomic constraint

$$\sigma(\mathbf{r}_1, \dots, \mathbf{r}_N) = 0. \tag{6.1}$$

Under a constraint, molecular dynamics calculations generate an ensemble in which the two independent conditions, $\sigma(\mathbf{r}) = 0$ and $\dot{\sigma} = \Sigma_i (\mathbf{p}_i/m_i) \cdot \nabla_i \sigma = 0$, are satisfied. As was demonstrated in Ref. 23, if $f(\mathbf{p}, \mathbf{r})$ is the equilibrium phase space distribution function of the unconstrained system, then the partition function of the constrained ensemble is

$$\Omega = \int d^N \mathbf{p} \, d^N \mathbf{r} Z(\mathbf{r}) f(\mathbf{p}, \mathbf{r}) \, \delta(\sigma(\mathbf{r})) \, \delta(\dot{\sigma}(\mathbf{p}, \mathbf{r})), \tag{6.2}$$

where

$$Z(\mathbf{r}) = \sum_{i=1}^{N} \frac{1}{m_i} \left(\frac{\partial \sigma}{\partial \mathbf{r}_i} \right)^2. \tag{6.3}$$

The motion of the system subject to Eq. (6.1) can be obtained via Gauss' principle of least constraint. The equations of motion are written in the form

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i(\mathbf{r}) - \lambda \nabla_i \sigma(\mathbf{r}) \tag{6.4}$$

or as a set of second order differential equations

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i(\mathbf{r}) - \lambda \nabla_i \sigma(\mathbf{r}), \tag{6.5}$$

where λ, the Lagrange multiplier, is to be replaced by a function of the phase space variables.

In order to derive an explicit form of the Lagrange multiplier λ, Eq. (6.1) is differentiated twice with respect to time, yielding

$$\frac{d^2}{dt^2} \sigma(\mathbf{r}) = \sum_j \nabla_j \sigma \cdot \ddot{\mathbf{r}}_j + \sum_{j,k} \nabla_j \nabla_k \sigma \cdot \cdot \dot{\mathbf{r}}_j \dot{\mathbf{r}}_k = 0. \tag{6.6}$$

Next, Eq. (6.5) is substituted into Eq. (6.6) and the resulting equation solved for λ, which gives

$$\sum_j \nabla_j \sigma \cdot \left[\frac{\mathbf{F}_j}{m_j} - \frac{\lambda}{m_j} \nabla_j \sigma(\mathbf{r}) \right] + \sum_{j,k} \nabla_j \nabla_k \sigma \cdot \cdot \dot{\mathbf{r}}_j \dot{\mathbf{r}}_k = 0,$$

$$\tag{6.7}$$

$$\lambda = \frac{\Sigma_j \mathbf{F}_j \cdot \nabla_j \sigma / m_j + \Sigma_{j,k} \nabla_j \nabla_k \sigma \mathbf{p}_j \mathbf{p}_k / (m_j m_k)}{\Sigma_n (\nabla_n \sigma)^2 / m_n}.$$

Substitution of Eq. (6.7) into Eqs. (6.4) yields the constrained equations of motion

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i \tag{6.8}$$

$$- \left[\frac{\Sigma_j \mathbf{F}_j \cdot \nabla_j \sigma / m_j + \Sigma_{j,k} \nabla_j \nabla_k \sigma \cdot \cdot \mathbf{p}_j \mathbf{p}_k / (m_j m_k)}{\Sigma_n (\nabla_n \sigma)^2 / m_n} \right] \nabla_i \sigma,$$

which are non-Hamiltonian and have the constraints $\sigma = 0$ and $\dot{\sigma} = 0$ as conservation laws. The compressibility associated with Eqs. (6.8) is[42]

$$\kappa = \sum_i \nabla_{\mathbf{p}_i} \cdot \dot{\mathbf{p}}_i$$

$$= - \frac{2 \Sigma_{i,j} \nabla_i \sigma / m_i \cdot \nabla_i \Sigma_j \nabla_j \sigma \cdot \mathbf{p}_j / m_j}{\Sigma_j (\nabla_j \sigma)^2 / m_j}$$

$$= - \frac{2 \Sigma_i \nabla_i \sigma \cdot \nabla_i \dot{\sigma} / m_i}{\Sigma_j (\nabla_j \sigma)^2 / m_j}$$

$$= - \frac{d}{dt} \ln \left[\sum_i (\nabla_i \sigma)^2 / m_i \right] \tag{6.9}$$

and the phase space metric, Eq. (2.15), takes the form

$$\sqrt{g} = e^{-w} = \exp \left\{ \ln \left[\sum_i (\nabla_i \sigma)^2 / m_i \right] \right\} = \sum_i \frac{1}{m_i} (\nabla_i \sigma)^2. \tag{6.10}$$

All phase space averages need to be performed with respect to a measure defined by this metric. However, this is just the factor in Eq. (6.3) required to properly weight the phase space according to the conservation laws $\sigma = 0$ and $\dot{\sigma} = 0$ obeyed by the equations of motion.[24–28] The above analysis, thus, shows that the weighting factor arises naturally from non-Hamiltonian equations of motion. As might be expected, the phase space can also be derived starting from a Hamiltonian description in generalized coordinates.[25,27,28] In practice, however, finding an appropriate set of generalized coordinates for an arbitrary set of constraint conditions can be nontrivial. The non-Hamiltonian formalism presented in this section shows that this necessity can be easily avoided and a considerably simpler non-Hamiltonian analysis employed.

VII. CONCLUSION

The recently introduced statistical theory of non-Hamiltonian systems has been applied to develop a procedure for constructing an appropriate generalization of Hamiltonian phase space analysis. Specifically, it has been demonstrated that only by combining the invariant measure, the conservation laws and a careful reduction of the phase space to the irreducible set can the partition function of these systems be properly constructed. Applications of the new formalism to isothermal isobaric MD, canonical MD, and systems with holonomic and nonholonomic constraints, have shown the approach is capable of predicting nontrivial phase space distributions. The applications also serve to illu-

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minate the deficiencies of older, less general, formalisms. Thus, the ability of the results presented in Ref. 14, and the techniques of differential geometry as applied to dynamical systems,[15–17] in general, to contribute to the understanding of the non-Hamiltonian equations of motion commonly employed in chemical physics, have been clearly demonstrated.

APPENDIX A

In this Appendix, a derivation of Eq. (2.12) is presented. This derivation is not new and can be found, for example, in Refs. 31 and 14. It is reproduced here for completeness.

By definition, the Jacobian given in Eq. (2.11) can be written as the determinant of a matrix $\mathbf{M}$ according to:

$$J(x_t;x_0) = \det(\mathbf{M}) = e^{\mathrm{Tr}(\ln \mathbf{M})}, \tag{A1}$$

where a familiar identity for the determinant has been used. The elements of the matrix $\mathbf{M}$ are $M_{ij} = \partial x_t^i / \partial x_0^j$. An equation of motion for $J(x_t;x_0)$ can be derived by computing the time derivative of both sides of Eq. (A1), which yields

$$\frac{dJ}{dt} = J\,\mathrm{Tr}\left(\mathbf{M}^{-1}\frac{d\mathbf{M}}{dt}\right) = J\sum_{i,j} M_{ij}^{-1}\frac{dM_{ji}}{dt}. \tag{A2}$$

The matrix elements of $\mathbf{M}^{-1}$ and $d\mathbf{M}/dt$ are

$$M_{ij}^{-1} = \frac{\partial x_0^i}{\partial x_t^j}, \quad \frac{dM_{ji}}{dt} = \frac{\partial \dot{x}_t^j}{\partial x_0^i}. \tag{A3}$$

Substituting these expressions into Eq. (A2), the equation of motion for J reduces to

$$
\begin{aligned}
\frac{dJ}{dt} &= J\sum_{i,j}\frac{\partial x_0^i}{\partial x_t^j}\frac{\partial \dot{x}_t^j}{\partial x_0^i}\\
&= J\sum_{i,j,k}\frac{\partial x_0^i}{\partial x_t^j}\frac{\partial \dot{x}_t^j}{\partial x_t^k}\frac{\partial x_t^k}{\partial x_0^i}\\
&= J\sum_{j,k}\delta_{jk}\frac{\partial \dot{x}_t^j}{\partial x_t^k} = J\sum_{i}\frac{\partial \dot{x}_t^i}{\partial x_t^i} = J\kappa(x_t)
\end{aligned}
\tag{A4}
$$

or

$$\frac{d}{dt}J(x_t;x_0) = J(x_t;x_0)\kappa(x_t). \tag{A5}$$

Since Eq. (2.9) represents an identity transformation at $t = 0$, it is clear that Eq. (A5) is subject to the obvious initial condition $J(x_0;x_0) = 1$. In addition, note that the Jacobian of the inverse transformation

$$\bar{J}(x_0;x_t) = \det\frac{\partial(x_t^0\cdots x_0^n)}{\partial(x_t^1\cdots x_t^n)} \tag{A6}$$

satisfies an equation of motion of the form

$$\frac{d}{dt}\bar{J}(x_0;x_t) = -\bar{J}(x_0;x_t)\kappa(x_t), \tag{A7}$$

which follows directly from the fact that $J\bar{J} = 1$ for all time, hence, $\bar{J}dJ/dt + Jd\bar{J}/dt = 0$ and can also be derived using the above procedure.

The Jacobian determines how the phase space volume transforms according to Eq. (2.10). More precisely, it determines how the phase space metric defined in Sec. II transforms:[15]

$$
\begin{aligned}
\sqrt{g_0(x_0)} &= \sqrt{g_t(x_t)}J(x_t;x_0)\\
\sqrt{g_t(x_t)} &= \sqrt{g_0(x_0)}\bar{J}(x_0;x_t)
\end{aligned}
\tag{A8}
$$

which is consistent with the conservation law stated in Eq. (2.15).

APPENDIX B

A harmonic oscillator coupled to a Nosé–Hoover thermostat was first considered by Hoover[3] as a case in which the phase space distribution generated by the dynamics is not the expected canonical distribution. It will be shown here that this is very likely due to the presence of undetected conservation laws. The equations of motion for the Nosé–Hoover oscillator (with the mass, frequency, temperature, and thermostat mass Q all set equal to 1):

$$\dot{x} = p \quad \dot{p} = -x - p_\eta p \quad \dot{\eta} = p_\eta \quad \dot{p}_\eta = p^2 - 1. \tag{B1}$$

Equations (B1) have an associated conserved energy:

$$H' = \tfrac{1}{2}(p^2 + x^2 + p_\eta^2) + \eta. \tag{B2}$$

If Eq. (B2) were the *only* conserved quantity, then, by the analysis of Sec. IV A, leading up to Eq. (4.8), a canonical distribution should result. However, as Fig. 10 shows, a canonical distribution is not generated, thereby suggesting that an additional conservation law exists that has not been taken into account. For Eqs. (B1), finding such a hidden conservation law is nontrivial. However, by modifying the equations slightly in such a way that they retain the same pathology, a complete analysis can be carried out.

Consider modifying the Nosé–Hoover equations slightly to read

$$\dot{x} = p - p_\eta x \quad \dot{p} = -x - p_\eta p \quad \dot{\eta} = p_\eta \quad \dot{p}_\eta = p^2 + x^2 - 2. \tag{B3}$$

The compressibility associated with Eqs. (B3) is $\kappa = -2p_\eta$ so that the metric becomes $\sqrt{g} = \exp(2\eta)$. In addition, Eqs. (B3) have the conserved energy

$$H' = \tfrac{1}{2}(p^2 + x^2 + p_\eta^2) + 2\eta. \tag{B4}$$

Again, if Eq. (B4) were the only conservation law, then, by the procedure of Sec. II, it would follow that Eqs. (B3) should generate a canonical distribution. The distribution generated by these equations is shown in Fig. 11, which clearly shows that a canonical distribution is *not* generated. Moreover, Fig. 11 closely resembles Fig. 10. In fact, there is another conservation law associated with Eqs. (B4), namely,

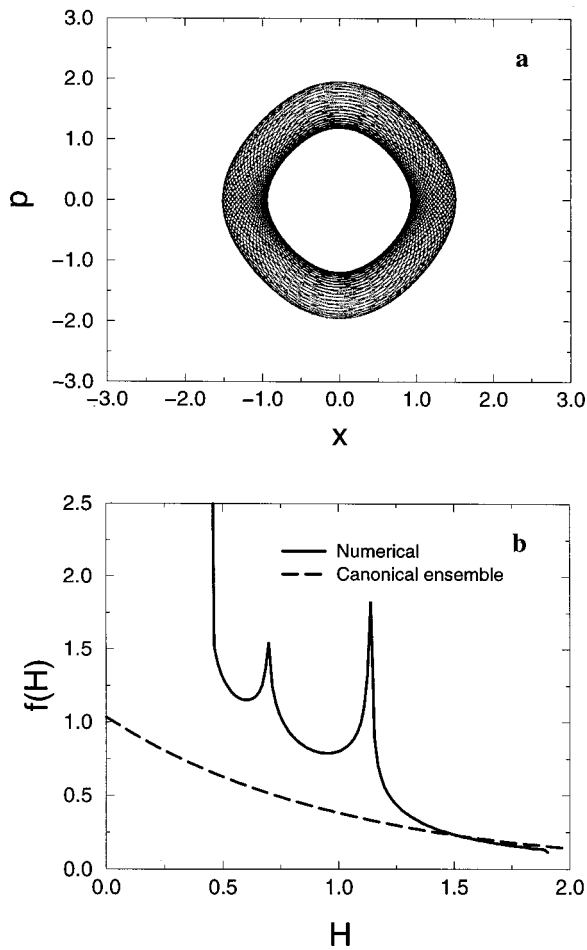$$K = \tfrac{1}{2}(x^2 + p^2)e^{2\eta}. \tag{B5}$$

FIG. 10. (a) The Poincaré section for a one-dimensional harmonic oscillator (see text) coupled to a Nosé–Hoover thermostat [$kT=1$, $p(0)=1$, $x(0)=1$, $Q=1$, $p_\eta(0)=1$ with a time step $\Delta t=0.02$]. (b) The distribution function of the harmonic oscillator action variable H (solid line) compared to the canonical ensemble distribution (dashed line).
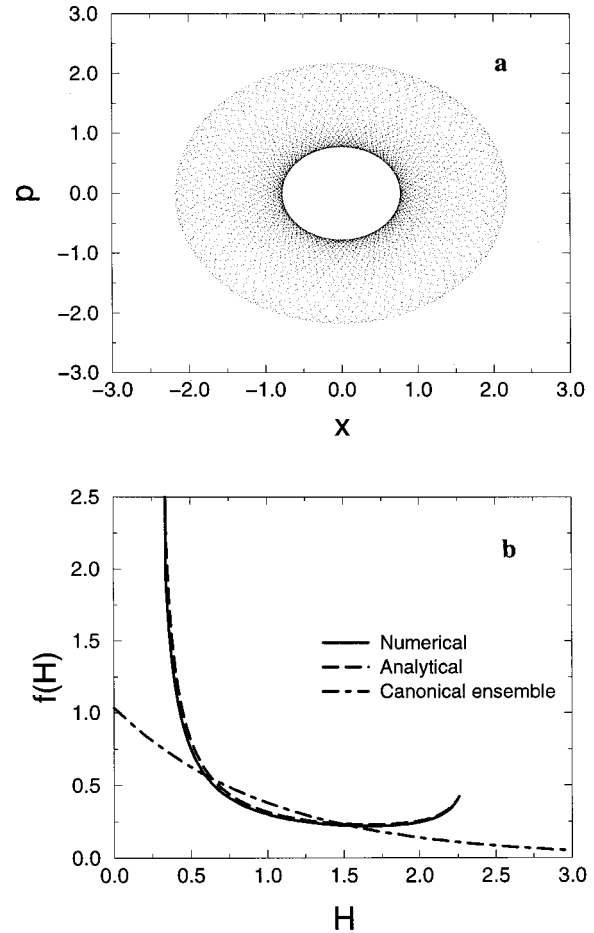

FIG. 11. (a) The Poincaré section for the harmonic oscillator (see text) coupled to the "modified" Nosé–Hoover thermostat [see Eqs. (B3)] with the same initial conditions as in Fig. 10. (b) The distribution function of the harmonic oscillator action variable H (solid line) compared to the analytical (dashed line) and the canonical ensemble (dot dashed line) distribution.

This can be shown straightforwardly by computing dK/dt and using the equations of motion. Taking into account Eq. (B5), the expression for the partition function becomes

$$\Omega(C_1, C_2) = \int dp \, dx \, dp_\eta \, d\eta \, e^{2\eta} \delta\left(\frac{1}{2}(p^2 + x^2 + p_\eta^2)\right.$$

$$\left. + 2\eta - C_1\right) \delta\left(\frac{1}{2}(x^2 + p^2)e^{2\eta} - C_2\right)$$

$$= \int dp \, dx \, dp_\eta \, d\eta \, e^{2\eta} \delta\left(H + \frac{1}{2}p_\eta^2 + 2\eta\right.$$

$$\left. - C_1\right) \delta(He^{2\eta} - C_2), \tag{B6}$$

where $H = (p^2 + x^2)/2$ is the physical Hamiltonian. Using the second δ function to integrate over η yields

$$\Omega(C_1, C_2) = \int dp \, dx \int dp_\eta \frac{1}{2H} \delta\left(H + \frac{1}{2}p_\eta^2 + \ln\frac{C_2}{H} - C_1\right). \tag{B7}$$

Finally, using the the remaining δ function to integrate over p_η leads to a distribution function $f(p,x)$ given by

$$f(p,x) = \frac{1}{H \sqrt{2\left(C_1 - H + \ln\frac{H}{C_2}\right)}}, \tag{B8}$$

which can also be regarded as a distribution function in the Hamiltonian H or the harmonic oscillator action variable.

In order to verify Eq. (B8), the distribution generated by the dynamics in Eqs. (B3) is compared to the analytical result in Fig. 11. The figure shows that the distribution is given correctly by Eq. (B8). Again, it is clear from this example that one needs to include all of the relevant conservation laws in order to determine the precise distribution that is generated by a given non-Hamiltonian system.

APPENDIX C

Consider the equations of motion,

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \frac{p_\epsilon}{W} \mathbf{r}_i \quad (i = 1, L),$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \frac{p_\epsilon}{W} \mathbf{p}_i - \frac{p_\eta}{Q} \mathbf{p}_i \quad (i = 1, L),$$

$$\dot{\mathbf{p}}_\gamma = -\frac{p_\epsilon}{W}\mathbf{p}_\gamma - \frac{p_\eta}{Q}\mathbf{p}_\gamma,$$

$$\dot{V} = \frac{dVp_\epsilon}{W}, \tag{C1}$$

$$\dot{p}_\epsilon = dV(P_{\text{int}} - P_{\text{ext}}) + \frac{\mathbf{p}_\gamma^2}{m_\gamma} - \frac{p_\eta p_\epsilon}{Q},$$

$$\dot{\eta} = \frac{p_\eta}{Q},$$

$$\dot{p}_\eta = \sum_{i=1}^{L}\frac{\mathbf{p}_i^2}{m_i} + \frac{\mathbf{p}_\gamma^2}{m_\gamma} + \frac{p_\epsilon^2}{W} - (dL+d+1)kT.$$

Here, d is the spatial dimensionality of the system and the variable $\mathbf{p}_\gamma$ is a d dimensional extended system variable (written as a momentum). The equations have the conserved quantity

$$H' = \sum_{i=1}^{L}\frac{\mathbf{p}_i^2}{2m_i} + \frac{\mathbf{p}_\gamma^2}{2m_\gamma} + \frac{p_\epsilon^2}{2W} + \frac{p_\eta^2}{2Q} + \phi(\mathbf{r},V)$$
$$+ (dL+d+1)kT\eta + P_{\text{ext}}V \tag{C2}$$

and phase space metric $\sqrt{g} = \exp[(dL+d+1)\eta]$.

Using the assumption of ergodicity, the metric and the conserved quantity, the partition function associated with the dynamics can be constructed,

$$\Delta = \int d\mathbf{p}_\gamma \int dp_\eta\, dp_\epsilon\, d\eta\, dV \int_{D(V)} d\mathbf{p}\, d\mathbf{r}\, \exp[(dL+d$$
$$+1)\eta]\delta(H'-E)$$
$$\Delta = \frac{\exp[E/kT]}{(dL+d+1)kT}\int d\mathbf{p}_\gamma \int dp_\eta\, dp_\epsilon\, dV \tag{C3}$$
$$\times \int_{D(V)} d\mathbf{p}\, d\mathbf{r}\, \exp\left[-\frac{H''}{kT}\right],$$

where

$$H'' = \sum_{i=1}^{L}\frac{\mathbf{p}_i^2}{2m_i} + \frac{\mathbf{p}_\gamma^2}{2m_\gamma} + \frac{p_\epsilon^2}{2W} + \frac{p_\eta^2}{2Q} + \phi(\mathbf{r},V) + P_{\text{ext}}V. \tag{C4}$$

Therefore, the dynamics generates positions and momentum in the NPT or isothermal–isobaric ensemble (avoiding, for the moment, a discussion of additional conservation laws which can be handled, as discussed in detail previously, by coupling the $\mathbf{p}_\gamma$, p_ϵ, and the $\mathbf{p}_i$ to independent thermostats and employing the Nosé–Hoover chain approach).

The connection of the preceding equations of motion, to those derived by Ciccotti *et al.*, Eqs. (5.24) can be made straightforwardly. If the force on the center-of-mass is zero ($\mathbf{F}_{\text{cm}} = 0$) and the equations of Ciccotti *et al.* are transformed from Cartesian coordinates to a set that includes the center of mass explicitly, then the new equations (directly above) are produced with $L = N-1$ and $\mathbf{p}_\gamma = \mathbf{p}_{\text{cm}}$, where N is the number of particles. In this case, the dynamics of Ciccotti *et al.* will generate the isothermal–isobaric distribution for an N

-1 rather than an N particle system because the center-of-mass has been unnaturally assigned the role of an extended system variable.

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[32] Strictly speaking, a volume element cannot be described as "Euclidean" or "non-Euclidean." Rather, it is the n-volume form $\tilde{\omega} = \sqrt{g}\,dx^1 \wedge \cdots \wedge dx^n$, which, mathematically, is Euclidean or non-Euclidean depending on whether the condition $\sqrt{g} = 1$ holds globally or not. The terminology of "Euclidean" or "non-Euclidean" volume elements is used only here in order to avoid the need to go into extensive mathematical detail. However, the strict meaning should be kept in mind.
[33] In this context, flat does not actually imply Euclidean. As an example, consider the metric of Minkowski space: system is actually given by

$$\mathbf{G} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

for which $\sqrt{|g|}=1$ but which is not the identity matrix. However, because the determinant is unity, the volume element has a "Euclidean-like" form, dx even though a non-Euclidean measure of length exists on the manifold.

[34] Again, the more mathematically precise statement would be one relating the phase space volume form at $t=0$ to that at an arbitrary time t as discussed in Ref. 13.

[35] The Riemann curvature tensor is related to the elements G_{ij} of the metric by

$$R^i_{jkl}=\frac{1}{2}G^{im}\left(\frac{\partial^2 G_{ml}}{\partial x^j \partial x^k}-\frac{\partial^2 G_{mk}}{\partial x^j \partial x^l}+\frac{\partial^2 G_{jk}}{\partial x^m \partial x^l}-\frac{\partial^2 G_{jl}}{\partial x^m \partial x^k}\right),$$

where G^{ij} is an element of the inverse metric matrix and a sum over m is implied. It is thus manifestly clear that for all $G_{ij}=$const, the curvature tensor will vanish since all of the partial derivatives will vanish. Since R^i_{jkl} transforms like a proper tensor, if all elements vanish in one coordinate system, they will vanish in all coordinate systems.

[36] The covariant form of the conservation law is $[(\partial/\partial t)+\mathcal{L}_\xi](f\tilde{\omega})=0$, where $\mathcal{L}_\xi$ is the Lie derivative and $\tilde{\omega}$ is the volume n form [cf. Eq. (5.68) in B. A. Dubrovin, A. T. Fomenko, and S. P. Novikov, *Modern Geometry—Methods and Applications,* Part I (Springer, New York, 1985).] Projection of this equation onto a specific set of phase space coordinates then leads to Eq. (2.10).

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