Non-Hamiltonian equilibrium statistical mechanics

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In this paper the equilibrium statistical mechanics of non-Hamiltonian systems is formulated introducing an algebraic bracket. The latter defines non-Hamiltonian equations of motion in classical phase space according to the approach introduced in Phys. Rev. E **64**, 056125 (2001). The Jacobi identity is no longer satisfied by the generalized bracket and as a result the algebra of phase space functions is not time translation invariant. The presence of a nonzero phase space compressibility spoils also the time-reversal invariance of the dynamics. The general Liouville equation is rederived and the properties of statistical averages are accounted for. The features of time correlation functions and linear response theory are also discussed.

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I. INTRODUCTION

Non-Hamiltonian dynamics has been introduced long ago in molecular dynamics simulations to achieve, by means of additional thermostat and/or barostats coordinates, the calculation of statistical averages in various ensemble [1–6]. Nowadays it is a key element in the design of modern simulation methods and it is worth to mention that also mixed quantum-classical system can be studied by a non-Hamiltonian approach [7–9].

In a previous paper [10], a general formalism for expressing non-Hamiltonian equations of motion with a conserved energy has been proposed [10] and it has been shown that already known non-Hamiltonian equations of motion, using thermostats and barostats, can be formulated in a unified way. It has also been suggested that one could invent new non-Hamiltonian phase space flows to attack some formidable problems like calculations on systems with coupling of different time or length scales. The necessary condition to such an achievement is the development of a consistent and coherent theory of statistical mechanics in the non-Hamiltonian case. Such a theory is proposed here considering only systems under thermodynamic equilibrium.

It must be mentioned that a formalism for the rigorous treatment of static averages has been already proposed in Refs. [11–13]. Anyhow some subtle points regarding time-translation and time-reversal properties of non-Hamiltonian dynamics remain to be clarified. As shown in the following the results of Refs. [11–13] that regards equilibrium systems can be reproduced and the above issues can be addressed by introducing a suitable algebraic bracket to treat non-Hamiltonian systems. The treatment of statistical mechanics by imposing an algebraic structure on phase space functions by means of the Poisson bracket in the Hamiltonian case is well established [14–17] and the approach presented here will be just a straightforward generalization. The use of a generalized bracket to formulate non-Hamiltonian dynamics has been sketched in Ref. [10]. Here, the formalism is brought to its natural completion, thus, showing that it is a legitimate tool for the study of non-Hamiltonian systems. The subtler feature is due to the fact that the generalized bracket does not satisfy the Jacoby relation so that the non-Hamiltonian algebra of phase space functions lacks time-translation invariance. It is worth to remark that, within the different context of mixed quantum-classical systems, the lack of time-translation invariance, as a consequence of the failure of the Jacobi identity, and its effects on the statistical mechanics, have been already addressed in the work of Ref. [9]. The bracket approach to equations of motion permits also to show that the presence of a nonzero compressibility of phase space spoils the time-reversal invariance of dynamical flows. The use of non-Hamiltonian dynamics to study dynamical quantities at equilibrium is a delicate matter and cannot be assessed on general ground. Anyway loosing in generality one can focus on a class of dynamical models where many relevant degrees of freedom, subjected to a quasi-Newtonian dynamics [3], are weekly coupled to few additional degrees of freedom. In such cases, there are techniques to show that the dynamics of the relevant degrees of freedom is meaningful, as it has been explicitly shown for the Nosé-Hoover dynamics [18]. Within this class of models it is sensible to calculate dynamical properties at equilibrium. For this reason non-Hamiltonian correlation functions and linear response theory are also treated.

The paper is organized as follows. In Sec. II a generalized algebraic bracket is introduced. This mathematical entity will be used consistently to define and discuss dynamics in phase space. In Sec. III the non-Hamiltonian Liouville equation is derived from the algebraic formalism, statistical averages are discussed and it is shown that when the compressibility is nonzero the dynamics is not time-reversal invariant. Dynamical features and correlation functions are discussed in Sec. IV. Linear response theory is treated in Sec. V. The last section is devoted to comments and conclusions.

II. NON-HAMILTONIAN DYNAMICS

Let the symbol $\mathbf{x}=(\mathbf{q},\mathbf{p})$ define the phase space point where generalized coordinates, by convention, come first and generalized momenta after. Then by defining an antisymmetric matrix $\mathcal{B}_{ij}=-\mathcal{B}_{ji}$, whose elements are general function of $\mathbf{x}$, it is possible to introduce a non-Hamiltonian bracket

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$\{\ldots,\ldots\}$ so that, given any two functions of phase space a and b, one has

$$\{a,b\}=\sum_{ij}^{2N}\frac{\partial a}{\partial x_i}\mathcal{B}_{ij}\frac{\partial b}{\partial x_j}, \tag{1}$$

where $2N$ is the dimension of phase space. Given a Hamiltonian $\mathcal{H}$, equations of motion can be postulated in the form

$$\dot{x}_k=\{x_k,\mathcal{H}\},\quad k=1,\ldots,2N. \tag{2}$$

Equations (2) with a constant antisymmetric matrix, written in block form as

$$\mathcal{B}=\begin{bmatrix} 0 & \mathbf{1} \\ -\mathbf{1} & 0 \end{bmatrix}, \tag{3}$$

are usually used to discuss the simplectic properties of canonical transformations [14]. Moreover, Eqs. (2) have the same structure used in the so called noncanonical Hamiltonian dynamics [15,16]. This structure is defined by a nonconstant antisymmetric matrix $\mathcal{B}$ that, in the noncanonical Hamiltonian case, can be derived from a well defined (noncanonical) transformation of coordinates in phase space.

Due to the antisymmetry of $\boldsymbol{\mathcal{B}}$, a time independent $\mathcal{H}$ will be a constant of motion under any phase space flow defined by the bracket of Eqs. (2):

$$\frac{d\mathcal{H}}{dt}=\{\mathcal{H},\mathcal{H}\}=\sum_{ij}^{2N}\frac{\partial \mathcal{H}}{\partial x_i}\mathcal{B}_{ij}\frac{\partial \mathcal{H}}{\partial x_j}=0. \tag{4}$$

The property given in Eq. (4) needs only the antisymmetry of $\boldsymbol{\mathcal{B}}$ but it is otherwise very general. This has been exploited in Ref. [10] to introduce a general nonsimplectic formalism for the definition of non-Hamiltonian flows in phase space. This formalism still keeps the definition of the equations of motion in Eqs. (2) with the bracket given in Eq. (1) but introduces a nonsimplectic form for the matrix $\boldsymbol{\mathcal{B}}$. It is clear that, when $\mathcal{H}$ is time independent, Eq. (4) remains valid for any nonsimplectic antisymmetric matrix $\boldsymbol{\mathcal{B}}$. Specific examples of a nonsimplectic antisymmetric matrix $\boldsymbol{\mathcal{B}}$ have been already presented in Ref. [10] In the following it is assumed that both $\mathcal{H}$ and the matrix $\boldsymbol{\mathcal{B}}$ are not explictly time dependent.

Although the bracket in Eqs. (2) points to a group theoretical expression for non-Hamiltonian flows in phase space it must be recognized that, in general, such a bracket does no longer satisfy the Jacobi relation, the most important property entering the definition of a Lie algebra. For a Lie algebra, or for Hamiltonian flows, Jacobi relation is

$$\mathcal{J}=\{a,\{b,c\}\}+\{b,\{c,a\}\}+\{c,\{a,b\}\}=0. \tag{5}$$

Noncanonical Hamiltonian dynamics satisfies Eq. (5) and it can be shown [15,16] that this implies

$$\sum_{m=1}^{2N}\left(\mathcal{B}_{im}\frac{\partial \mathcal{B}_{jk}}{\partial x_m}+\mathcal{B}_{km}\frac{\partial \mathcal{B}_{ij}}{\partial x_m}+\mathcal{B}_{jm}\frac{\partial \mathcal{B}_{ki}}{\partial x_m}\right)=0,$$
$$i,j,k=1,\ldots,2N. \tag{6}$$

Jacobi identity, either in the form of Eq. (5) or in the form of Eqs. (6), basically express an integrability condition on the dynamical algebra. In other words, when $\mathcal{J}=0$ the algebra defined by the bracket is invariant under time translations. Instead non-Hamiltonian dynamics is defined by

$$\mathcal{J}\neq 0. \tag{7}$$

Equation (7) says that the laws of motion, given in Eqs. (2), change the algebraic relations defined by the bracket in Eq. (1), i.e., the algebra is not invariant under time translations. The nonintegrability or lack of time-translation invariance in phase space can be loosely thought of as a kind of curvature but care must be taken because the treatment of phase space as a Riemannian space is not clear from this point of view [15]. A Riemannian treatment of phase space can, nevertheless, be very useful providing a proper treatment of the stability of dynamical systems. See, for example, the preprints in Ref. [19].

To simplify future reference an algebra for which Eq. (7) holds will be called non-Hamiltonian. To unveil the features of the non-Hamiltonian algebra it is worth to consider again the Jacobi relation between the phase space variables a, b, and $\mathcal{H}$, the Hamiltonian itself,

$$\{a,\{b,\mathcal{H}\}\}+\{\mathcal{H},\{a,b\}\}+\{b,\{\mathcal{H},a\}\}=\mathcal{R}. \tag{8}$$

A direct calculation shows that

$$\mathcal{R}=\sum_{i,j,k,n}\frac{\partial a}{\partial x_i}\frac{\partial b}{\partial x_k}\frac{\partial \mathcal{H}}{\partial x_n}\left(\mathcal{B}_{ij}\frac{\partial \mathcal{B}_{kn}}{\partial x_j}+\mathcal{B}_{nj}\frac{\partial \mathcal{B}_{ik}}{\partial x_j}+\mathcal{B}_{kj}\frac{\partial \mathcal{B}_{ni}}{\partial x_j}\right). \tag{9}$$

From Eq. (9) one gets

$$\{\{a,b\},\mathcal{H}\}=\{\dot{a},b\}+\{a,\dot{b}\}+\mathcal{R}, \tag{10}$$

that can also be written as

$$\frac{d}{dt}\{a,b\}=\{\dot{a},b\}+\{a,\dot{b}\}+\mathcal{R}. \tag{11}$$

Equation (11) shows that a non-Hamiltonian algebra is not invariant under time translation. A direct consequence of Eq. (11) is that the non-Hamiltonian bracket of two constant of motion is no longer a constant of motion.

The phase space flow defined by means of Eq. (1) might have a nonzero phase space compressibility κ [2–5]

$$\kappa=\sum_{ij}^{2N}\frac{\partial \mathcal{B}_{ij}}{\partial x_i}\frac{\partial \mathcal{H}}{\partial x_j}. \tag{12}$$

The compressibility is useful to characterize the statistical mechanical properties [11–13]. In the following, according to the point of view given in Ref. [15], the phase space will be considered an Euclidean space (i.e., without a metric) and *flat* even using canonical generalized coordinates. In fact the curvilinear abscissa along a general phase space path has no clear physical meaning and the concept of metric is meaningful only in Lagrangian configuration space. Phase space in canonical coordinates is *flat* according to a group theoretical meaning (i.e., translations with respect to different coordinate axis commute) and Euclidean axis can be defined. When a noncanonical transformation is applied translations with respect to different coordinate axis could no longer commute and phase space can be considered *curved*. From this perspective there is still no need to introduce a metric, but the geometrical measure of phase space can be introduced. Considering a general transformation $\mathbf{x}\rightarrow\mathbf{x}'$ the integration element changes according to

$$d\mathbf{x}=\frac{|\partial\mathbf{x}|}{|\partial\mathbf{x}'|}d\mathbf{x}'=Jd\mathbf{x}', \tag{13}$$

where the Jacobian J describes all the *geometric* effects of the transformation of coordinates. It is worth to remark that the general bracket in Eq. (1) is already known to be covariant with respect to canonical [14] and noncanonical [15,16] transformation of coordinates. If the flow in time is considered then another Jacobian J_t can be defined

$$J_t=\left|\frac{\partial x(t)}{\partial x(0)}\right|, \tag{14}$$

arising from the relation between the coordinates at time 0 and the *same kind* of coordinates at time t. In the following section it will be shown, in agreement with the results of Refs. [11–13], how the dynamical properties described by J_t affects the *statistical* weight of phase space.

III. STATISTICAL MECHANICS

In molecular dynamics calculations what is typically achieved is the knowledge of a dynamical quantity, say a, along the computed time t spanning the total interval T. Given this time averages are calculated as

$$\langle a\rangle=\frac{1}{T}\int_0^T dt\, a(t). \tag{15}$$

The connections of the time average to the statistical mechanics of Gibbs, treating ensemble averages, is usually assumed by invoking the ergodic hypothesis and assuming that the limit $T\rightarrow\infty$ is numerically achieved. Then Eq. (15) is, by hypothesis, equal to the ensemble average

$$\langle a\rangle=\int dx^{2N}\rho(\mathbf{x})a(\mathbf{x}(T)). \tag{16}$$

To write Eq. (16) a distribution function ρ not depending explicitly on time has been considered, assuming in practice an equilibrium ensemble. The eventual presence of the Jacobian of Eq. (13) can be reabsorbed in the definition of $\rho(\mathbf{x})$ and its presence will be no longer explicitly considered. Consistency requires that both $\mathcal{H}$ and $\mathcal{B}$ must be time independent.

Equation (16) describes what is usually called the Heisenberg picture of statistical mechanics [17] according to which ρ is stationary, acting as a weight over initial conditions, while the dynamical variables evolve in time. The equilibrium condition ensures that upon averaging over initial condition the time dependence under the integral disappears and the equilibrium average in the left-hand side (lhs) of Eq. (16) is stationary.

To check the statistical ensemble Eq. (16) can be rewritten in the Schrödinger picture [17] according to which phase space variables like a are fixed in time while the ensemble distribution function ρ evolves in time. To do this it is useful, using Eqs. (2) and the non-Hamiltonian bracket, to introduce the Liouville operator

$$i\hat{\mathcal{L}}=\mathcal{B}_{ij}\frac{\partial\mathcal{H}}{\partial x_j}\frac{\partial}{\partial x_i}=\{\ldots,\mathcal{H}\}. \tag{17}$$

Reminding that in the present case $\boldsymbol{\mathcal{B}}$ and $\mathcal{H}$ are not explicitly time dependent the propagator can be defined as

$$\hat{G}(T)=\exp(i\hat{\mathcal{L}}T). \tag{18}$$

The propagator allows to advance in time general phase space functions $a(\mathbf{x})$ representing microscopic dynamical variable:

$$a(\mathbf{x}(T))=\hat{G}(T)a(\mathbf{x}(0)). \tag{19}$$

Equation (16) then can be rewritten as

$$\langle a\rangle=\int dx^{2N}\rho(\mathbf{x})\hat{G}(T)a(\mathbf{x}(0)\}. \tag{20}$$

To get the Schrödinger picture from Eq. (20) the action of the propagator $\hat{G}(T)$ must be transferred from a to ρ which amounts in practice to the calculation of the adjoint $\hat{G}^{\dagger}(T)$. It is known that the adjoint can be calculated integrating by parts [20]. If there is a nonzero compressibility κ of phase space, as given in Eq. (12), then by expanding in series $\hat{G}(T)$ under the integral and integrating by parts, assuming the vanishing of the boundary terms, one finds that the expression of the adjoint $\hat{G}^{\dagger}(T)$ acting on ρ involves the compressibility κ (i.e., the Liouville operator $i\hat{\mathcal{L}}$ is not Hermitian)

$$\hat{G}^{\dagger}(T)=\exp[-T(i\hat{\mathcal{L}}+\kappa)]. \tag{21}$$

Equation (21) defines the adjoint of the Liouville operator

$$(i\hat{\mathcal{L}})^{\dagger}=-i\hat{\mathcal{L}}-\kappa. \tag{22}$$

Equation (22) shows that, besides the lack of time-translational invariance, when $\kappa\neq 0$ the flow in phase space is not even time reversible. By defining a time evolving distribution function

$$\rho(\mathbf{x}(T))=\hat{G}^{\dagger}(T)\rho(\mathbf{x}(0)). \tag{23}$$

Equation (16) is finally rewritten as

$$\langle a\rangle=\int dx^{2N}[\hat{G}^{\dagger}(T)\rho(\mathbf{x}(0))]a(\mathbf{x}(0)). \tag{24}$$

It is easy to recognize in Eq. (23) the generalized Liouville equation

$$\frac{\partial\rho}{\partial t}=-i\hat{\mathcal{L}}\rho-\kappa\rho. \tag{25}$$

Equation (23) has been derived starting from the non-Hamiltonian algebraic bracket in phase space given in Eq. (1). Equation (23) defines a non-Hamiltonian flows for the distribution function ρ if the bracket in Eq. (1) does not satisfy the Jacobi relation, Eq. (5) or Eq. (6). A non-Hamiltonian Liouville equation, in a somewhat different form than that of Eq. (25), has been suggested in Refs. [11,12] and extensively used in Ref. [13]. Yet the form of Eq. (25) is preferable both because it is known since 1838 from the work of Liouville, see Refs. [21–23] for general discussions and comments also valid for the nonequilibrium steady state case (not treated in the present work), and because Eq. (25) has been easily derived in the present work starting from the non-Hamiltonian bracket and without entering too difficult and subtle discussion on the, very peculiar, geometry of phase space.

A nonzero compressibility has important effects on the statistical mechanics. In fact it is clear that if $\kappa\neq 0$ then the Liouville operator is not Hermitian. Moreover, the presence of a nonzero κ modifies the statistical measure of phase space determining, in general, the ensemble in which averages are calculated. In the following, non-Hamiltonian statistical averages are discussed.

The generalized Liouville Eq. (25) ensures the invariance in time of the normalization

$$\frac{d}{dt}\int d\mathbf{x}\rho(\mathbf{x})=0. \tag{26}$$

From Eq. (25) is also easy to establish the total time variation of ρ,

$$\frac{d\rho}{dt}(\mathbf{x})=-\kappa(\mathbf{x})\rho(\mathbf{x}). \tag{27}$$

The distribution function in phase space can be derived by integrating with respect to time Eq. (27). So doing between T_0 to T one finds

$$\log\rho(\mathbf{x}(T))-\log\rho(\mathbf{x}(T_0))=-\int_{T_0}^{T}dt\,\kappa(\mathbf{x}(t)). \tag{28}$$

As shown in Refs. [11,12] the compressibility is related to the Jacobian J_t associated to the phase space flow by an equation similar to Eq. (28)

$$\frac{d}{dt}\log J_t(\mathbf{x})=\kappa(\mathbf{x}). \tag{29}$$

Equation (29) ensures that the compressibility is exactly integrable with respect to time. Let w indicate the primitive function of κ. When Eq. (29) is integrated from 0 to T it gives

$$\log J_t(\mathbf{x}(T))-\log J_t(\mathbf{x}(0))=w(\mathbf{x}(T))-w(\mathbf{x}(0)). \tag{30}$$

It is worth to remark that Eq. (30) has been derived under the assumption that both $\mathcal{H}$ and $\boldsymbol{\mathcal{B}}$ are time independent. This condition implies that the compressibility in Eq. (12) and its primitive function w do not depend explictly on time, as it must be in an equilibrium ensemble.

By definition $J_t(0)=1$ and, thus, it follows that $w(0)=0$. Thus setting the time origin $T_0=0$ in Eq. (28) the simple form of the distribution function given in Refs. [11–13] is obtained

$$\rho(\mathbf{x}(T))=\rho(\mathbf{x}(0))\exp[-w(\mathbf{x}(T))]. \tag{31}$$

The distribution in Eq. (31) is consistently derived from the integration of the Liouville equation, Eq. (25), by setting $T_0=0$, i.e., fixing once and for all the time origin and, thus, breaking time-translational invariance. As a matter of fact it has already been shown in Eq. (11) that the absence of time translational invariance is a subtle consequence of the failure of the Jacoby relation in the non-Hamiltonian case.

By putting the distribution function in the form given in Eq. (31) back into the Liouville equation, Eq. (25), and doing simple algebra one can put the Liouville equation into the equivalent form suggested in Refs. [11–13], but the non-Hermitian property of the Liouville operator is then masked.

From the condition of derivation of Eq. (31) it is clear that ρ is not explicitly time dependent, i.e., $\partial\rho/\partial t=0$, and the Liouville equation can be written as

$$-[i\hat{\mathcal{L}}\rho+\kappa]\rho(\mathbf{x})=0, \tag{32}$$

so that Eq. (31) defines consistently an equilibrium ensemble.

To characterize the equilibrium ensemble it is important to fix the form of the distribution function at time $T=0$. This can be achieved by reminding that the time independent Hamiltonian $\mathcal{H}$ is conserved by the non-Hamiltonian bracket in Eqs. (2). Yet following the analysis of Ref. [13] it is also to be considered that if $\alpha_r=\alpha_r(\mathbf{x})$, with $r=1,\ldots,n$, are microscopic constant of motion, i.e., $\{a,\mathcal{H}\}=0$, then any function of the form $F(\mathcal{H},\alpha_1,\ldots,\alpha_n)$ will be a solution of the Liouville equation [17]. However, the Hamiltonian $\mathcal{H}$ is qualitatively different from all the other microscopic constant of motion. Simple algebraic definitions, as $\dot{\alpha}_r=0$, does not allow to establish a thermodynamic (macroscopic) ensemble. Instead the hypothesis of statistical mechanics is that only special microscopic functions survives the process of averaging over statistical fluctuations. These functions, like $\mathcal{H}$, and for some systems the total linear momentum **P** and total angular momentum **L**, are connected to the symmetries of the system under study. As suggested in Ref. [13] other constant of motion could turn out to be important to define a macroscopic ensemble. Yet there is no general method to discover such quantities and one must check in each single case. Following the work of Ref. [13], if Eqs. (2) are ergodic and c_i, $i=1,\ldots,k$ are statistically *relevant* conserved quantity beside $\mathcal{H}$, the form to be expected from solutions of Eq. (27) is

$$\rho(\mathbf{x}) = \delta(\mathcal{H}-E)\prod_{i=1}^{k}\delta(c_i-\tilde{c}_i)\exp[-w(x)]. \tag{33}$$

As remarked in Ref. [13], Eq. (33) must be used to check the statistical ensemble provided by the specific non-Hamiltonian phase space flow employed. As already shown in Refs. [11–13] the Jacobian J_t associated to flow in time enters explicitly, through w, into the definition of the distribution function and this result has been rederived in this section using the generalized Liouville equation in the form of Eq. (25).

IV. DYNAMICAL PROPERTIES

General non-Hamiltonian equations of motion drastically change the dynamical properties of a system. Yet there is a class of dynamical systems, which is the one actually exploited in molecular dynamics simulations, where many relevant degrees of freedom are weakly coupled to few additional coordinates. These systems are usually referred as extended systems [1]. Nosé-Hoover thermostat [2–4] and Nosé-Hoover chains [5] are well known examples. For this class of systems the equations of motion for the relevant coordinates are in quasi-Newtonian form and in accordance with the analysis of Ref. [3] their dynamics can have a realistic meaning. In particular the validity, in the thermodynamic limit, of equilibrium correlation functions has been explicitly shown for the case of the Nosé-Hoover thermostat in Ref. [18]. Given the existence of this class of systems, which is in practice very important, it is also important to formulate the features of non-Hamiltonian correlation functions and linear response theory. Thus, in this and in the following section dynamical properties are discussed.

It is worth to remark that the absence of time-translation invariance, shown by Eq. (11), has subtle but important effects. As a matter of fact applying the non-Hamiltonian propagator given in Eq. (18) to $\{a,b\}$ one gets

$$\hat{G}(T)\{a(0),b(0)\} = \{a(T),b(T)\} + O(T). \tag{34}$$

Equation (34) is rather boring in some sense because it means that time-translation invariance of the bracket is valid only to order $O(T)$ in time. There is no simple way to evaluate the $O(T)$ terms in the right-hand side (rhs) of Eq. (34). To show this the particular case when c_1 and c_2 are constants of motion will be considered as an example

$$\{c_i,\mathcal{H}\} = i\hat{\mathcal{L}}c_i = 0, \quad i=1,2. \tag{35}$$

Equation (35) can also be expressed as $c_i(T)=c_i(0)$, $i=1,2$. It is easy to find that

$$(i\hat{\mathcal{L}})^n\{c_1,c_2\} = \frac{d^{n-1}}{dt^{n-1}}\mathcal{R}, \quad n=1,\ldots,\infty, \tag{36}$$

so that propagating forward in time the bracket of the two constants of motion one obtains

$$\hat{G}(T)\{c_1(0),c_2(0)\} = \{c_1(T),c_2(T)\} + \sum_{n=1}^{\infty} T^n \frac{d^{n-1}}{dt^{n-1}}\mathcal{R}. \tag{37}$$

As for the compressibility κ one can show it affects the properties of correlation functions. In fact, when $\kappa \neq 0$ the Liouville operator is not a Hermitian operator but its adjoint is given by $i\hat{\mathcal{L}}^\dagger = -i\hat{\mathcal{L}} - \kappa$. This simple equation implies features of the correlation functions that are different from the Hamiltonian case. In the case of a static average, we have

$$\langle a\dot{b}\rangle = -\langle \dot{a}b\rangle - \langle \kappa ab\rangle, \tag{38}$$

while if the dynamic is Hamiltonian one has $\langle a\dot{b}\rangle = 0$. In an analogous manner, one can derive that the stationary property of the correlation function is no longer valid

$$\frac{d}{ds}\langle b(t+s)a(s)\rangle = -\langle \kappa b(t+s)a(s)\rangle. \tag{39}$$

It is worth to remark that, despite Eq. (39), for some extended systems the stationarity of the correlation function of relevant dynamical properties might not be ruined. To show this one can take as example a system coupled to a Nosé-Hoover [2–4] thermostat (yet the discussion will be also valid for coupling to Nosé-Hoover chains [5]). Let $m_i, \mathbf{q}_i, \mathbf{p}_i$, $i=1,\ldots,n$ be masses, coordinates and momenta of a N-particle systems. $\Phi(\{q\})$ will be the interaction potential. η, p_η are the thermostat variables and m_η the associated inertial parameters. The conserved Nosé Hamiltonian is

$$\mathcal{H}_N = \sum_{i=1}^{n}\frac{\mathbf{p}_i^2}{2m} + \frac{p_\eta^2}{m_\eta} + \Phi(\{q\}) + 3nk_BT\eta = \mathcal{H}_T + 3nk_BT\eta, \tag{40}$$

where T is the external temperature and k_B Boltzmann constant. The distribution function in the extended phase space takes the form

$$\rho_N = \delta(\mathcal{H}_N - E)\exp(-\beta\mathcal{H}_T), \tag{41}$$

and it is an even function of the momenta $\mathbf{p}_i$ and p_η. Instead the compressibility is and odd function of the momentum p_η, $\kappa = -3Np_\eta/m_\eta$. So if a and b in Eq. (39) are functions only of $(\{\mathbf{q}\},\{\mathbf{p}\})$ then the rhs in Eq. (39) is null on average.

V. LINEAR RESPONSE THEORY

To derive the formalism of linear response theory one as usual considers that a system with Hamiltonian $\mathcal{H}_0$ is perturbed at time $t=0$ by an external time dependent force $F(t)$ coupling to the dynamical variable a. The perturbation can be represented by the interaction Hamiltonian $\mathcal{H}_I$

$$\mathcal{H}_I = -aF(t). \tag{42}$$

The total Hamiltonian governing the motion will be

$$\mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}_I(t), \tag{43}$$

and it will no longer be a constant of motion, being explicitly time dependent. Yet using the algebraic non-Hamiltonian bracket one could introduce the Liouville operator

$$i\hat{\mathcal{L}}=\mathcal{B}_{ij}\frac{\partial\mathcal{H}_0}{\partial x_j}\frac{\partial}{\partial x_i}-F(t)\mathcal{B}_{ij}\frac{\partial a}{\partial x_j}\frac{\partial}{\partial x_i}=i\hat{\mathcal{L}}_0+i\hat{\mathcal{L}}_a. \quad (44)$$

The average of $b(t)$ is related to $F(t)$ by

$$\langle b(t)\rangle=\int_0^t ds \quad \chi(t-s)F(s), \quad (45)$$

$\chi(t)$ is the so called response function and it can be evaluated starting from

$$\langle b(t)\rangle=\int dx\, b(x)\rho(x,t). \quad (46)$$

Assuming that the external field is small the distribution function can be written as an unperturbed plus a small perturbed part

$$\rho=\rho_0+\delta\rho. \quad (47)$$

When $\hat{\mathcal{L}}$ is not Hermitian, the equation of motion for the distribution function is given by Eq. (25) and under the effect of a time dependent perturbation the compressibility is explicitly time dependent

$$\kappa=\frac{\partial\mathcal{B}_{ij}}{\partial x_i}\frac{\partial\mathcal{H}_0}{\partial x_j}-F(t)\frac{\partial\mathcal{B}_{ij}}{\partial x_i}\frac{\partial a}{\partial x_j}=\kappa_0+\kappa_I(t). \quad (48)$$

The Liouville equation to first order in the perturbation is then

$$\frac{\partial\delta\rho}{\partial t}=-i\hat{\mathcal{L}}_0\delta\rho-i\hat{\mathcal{L}}_I\rho_0-\kappa_0\delta\rho-\kappa_I(t)\rho_0. \quad (49)$$

The solution is given by

$$\delta\rho(t)=\int dt_1F(t)\exp[-(t-t_1)(i\hat{\mathcal{L}}_0+\kappa_0)] \times\left(\{\rho_0,a\}+\frac{\partial\mathcal{B}_{ij}}{\partial x_i}\frac{\partial a}{\partial x_j}\rho_0\right). \quad (50)$$

The response function is

$$\chi(t)=\int dx\, b(x)\exp[-t(i\hat{\mathcal{L}}_0+\kappa_0)] \times\left(\{\rho_0,a\}+\frac{\partial\mathcal{B}_{ij}}{\partial x_i}\frac{\partial a}{\partial x_j}\rho_0\right). \quad (51)$$

Now if the time dependence is transferred on b the compressibility κ disappear from the propagator and one gets

$$\chi(t)=-\int dx\rho_0\{b(t),a\}=-\langle\{b(t),a\}\rangle_0, \quad (52)$$

where the term $b(t)(\partial\mathcal{B}_{ij}/\partial x_i)(\partial a/\partial x_j)\rho_0$ has been canceled by a term of opposite sign appearing when going, by integration by parts, from $b(t)\{\rho_0,a\}$ to $\rho_0\{b(t),a\}$. Equation (52) shows a form of the response function equal to the one of the Hamiltonian case. Yet the simple form of Eq. (52) is quite rigid. The derivation has already shown that additional terms, containing the derivatives of $\mathcal{B}$, appear when doing integration by parts. As a results other forms of the response functions, usually derived within Hamiltonian dynamics, may not be valid within a non-Hamiltonian algebra and must be checked case by case.

VI. CONCLUSIONS

In this paper it has been shown that the equilibrium statistical mechanics of non-Hamiltonian systems can be consistently and thoroughly treated by means of a generalized bracket defining flows in phase space. The bracket does not satisfy the Jacoby relation and, thus, it defines an algebra that is not invariant under time translations. Phase space compressibility and the standard non-Hamiltonian Liouville equation have been easily derived from the bracket form of the equations of motion. The compressibility breaks the time-reversal invariance of the dynamics and modifies the statistical weight of phase space.

The stationary property of general correlation functions is broken by the compressibility. Yet in some relevant cases correlations of a subset of the coordinates might not be affected by this problem. A specific form of the response function in the linear regime has also been derived.

The statistical mechanics of non-Hamiltonian systems at equilibrium can be studied by different mathematical languages. Some authors have used a metric in phase space and a peculiar form of the Liouville equation. In their approach the equations of motion for the dynamical variables must be provided by some other means. In this paper the generalized Liouville equation, in a form known since Liouville's original work, and the phase space compressibility have been used. It has been shown that when the physics, symmetries and conserved quantities, are carefully considered the results obtained using the two languages are equivalent. The main difference is that in the approach presented in this paper all the statistical ingredients naturally arise from the formalism of the non-Hamiltonian equations of motion. For such a reason the algebraic bracket formalism promises to be a more flexible tool to invent various types of dynamics with the statistical mechanics under control.

Further analysis is required to investigate the conditions of applicability of general non-Hamiltonian dynamics to calculate transport coefficients or to treat nonequilibrium ensembles.

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[1] H.C. Andersen, J. Chem. Phys. **72**, 2384 (1980).
[2] S. Nosé, Mol. Phys. **52**, 255 (1984).
[3] S. Nosé, Prog. Theor. Phys. **103**, 1 (1991).
[4] W.G. Hoover, Phys. Rev. A **31**, 1695 (1985).
[5] G.J. Martyna, M.L. Klein, and M. Tuckerman, J. Chem. Phys. **97**, 2635 (1992).
[6] P. Klein, Modell. Simul. Mater. Sci. Eng. **6**, 405 (1998).
[7] R. Kapral and G. Ciccotti, J. Chem. Phys. **110**, 8919 (1999).
[8] S. Nielsen, R. Kapral, and G. Ciccotti, J. Chem. Phys. **112**, 6543 (2000).
[9] S. Nielsen, R. Kapral, and G. Ciccotti, J. Chem. Phys. **115**, 5805 (2000).
[10] A. Sergi and M. Ferrario, Phys. Rev. E **64**, 056125 (2001).
[11] M. Tuckerman, C.J. Mundy, and M.L. Klein, Phys. Rev. Lett. **78**, 4103 (2001).
[12] M. Tuckerman, C.J. Mundy, and G.J. Martyna, Europhys. Lett. **45**, 149 (1999).
[13] M.E. Tuckerman, Y. Liu, G. Ciccotti, and G.L. Martyna, J. Chem. Phys. **115**, 1678 (2001).
[14] H. Goldstein, *Classical Mechanics*, 2nd ed. (Addison-Wesley, London, 1980).
[15] J.L. McCauley, *Classical Mechanics* (Cambridge University Press, Cambridge, 1977).
[16] P.J. Morrison, Rev. Mod. Phys. **70**, 467 (1998).
[17] R. Balescu, *Equilibrium and Non Equilibrium Statistical Mechanics* (Wiley, New York, 1975).
[18] D.J. Evans and B.L. Holian, J. Chem. Phys. **83**, 4069 (1985).
[19] G. Sardanashvily, e-print arXiv;nlin.CD/020331; e-print arXiv.nlin.CD/0201060.
[20] P. Dennery and Krzywicki, *Mathematics for Physicists* (Dover, New York, 1996).
[21] D.J. Evans, D.J. Searles, B.L. Holian, H.A. Posch, and G.P. Morris, J. Chem. Phys. **108**, 4351 (1998).
[22] W.G. Hoover, D.J. Evans, H.A. Posch, B.L. Holian, and G.P. Morris, Phys. Rev. Lett. **18**, 4103 (1998).
[23] W.G. Hoover, J. Chem. Phys. **109**, 4164 (1998).