Generalized bracket formulation of constrained dynamics in phase space

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A generalized bracket formalism is used to define the phase space flow of constrained systems. The generalized bracket naturally subsumes the approach to constrained dynamics given by Dirac some time ago. The dynamical invariant measure and the linear response of systems subjected to holonomic constraints are explicitly derived. In light of previous results, it is shown that generalized brackets provide a simple and unified view of the statistical mechanics of non-Hamiltonian phase space flows with a conserved energy.

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I. INTRODUCTION

The use of mechanical constraints in molecular dynamics simulations has a fundamental importance for both modeling complex systems and dealing with rare events [1–4], see Ref. [5] for a recent application. Constraints are also mandatory in molecular dynamics simulations with potentials derived from density functional theory [6]. Despite their importance, it is reasonable to expect that the above-mentioned examples do not exhaust the range of possible applications of constraints in both theory and simulations. To this end, general and simple mathematical formalisms can provide the language to attack new problems. The aim of the present paper is to suggest such a formalism treating constrained dynamics in phase space by means of generalized antisymmetric brackets.

Some time ago, Dirac defined a generalized bracket to treat constraints [7,8]. Its main concern was to quantize systems with constraints arising from a singular Hessian. His approach was successively adopted by Anderson and Bergman to study systems with gauge symmetries [9]. Systems with a singular Hessian naturally emerge in relativistic mechanics and field theory [10–12]. In these cases, the singularity is shown to be related to gauge invariance [12]. Ordinary nonrelativistic constrained systems, such as those used to simulate molecular systems, do not usually have a singular Hessian. For example, one could consider a systems of N nonrelativistic point charges interacting via Coulombic (plus eventually Lennard-Jones) potentials, with constraints to describe molecular topology or a rarely sampled configuration. For such systems, one does not need to be concerned with Dirac classification of constraints or with gauge invariance. Thus, few applications of Dirac's approach to classical nonrelativistic systems are found in the literature. Some examples are the use of Dirac's theory to study biophysical systems [13,14] and to formulate algorithms for holonomic constraints in molecular dynamics simulation [15,16]. Nevertheless, Dirac generalized bracket provides a phase space point of view for the constrained dynamics of classical nonrelativistic systems (for which gauge symmetry has a minor importance) that can still be useful.

In the present paper the emphasis is put on the bracket formulation of constrained dynamics as the more natural context in which statistical mechanics can be formulated. In previous papers [17,18] an antisymmetric bracket formalism, describing in a unified way non-Hamiltonian phase space flows commonly used in molecular dynamics simulations [19–23], has been provided and the statistical mechanics of non-Hamiltonian systems has been easily addressed [24–30]. Linear response theory, correlations functions, and the subtle properties of the generalized phase space algebra, analogous to the ones of quantum-classical algebra [31–33], have also been discussed [18]. Here it is shown how the generalized bracket formalism of Refs. [17,18] can be easily extended to provide a formulation of the dynamics, equilibrium statistical mechanics, and linear response theory of systems with mechanical constraints. The key idea has been to write the Dirac bracket in terms of the simpler and more general bracket introduced in Refs. [17,18], with the rest following by means of algebraic manipulations. Thus, the main result is the definition of a simple language to formulate constrained phase space flows and their statistical mechanics which is unified with the formalism of non-Hamiltonian flows with a conserved energy. Extensions to quantum-classical systems are also straightforward [34].

The paper is organized as follows: in Sec. II the properties of the generalized bracket are briefly summarized; in Sec. III equilibrium statistical mechanics and linear response theory are discussed in a form useful for other sections; in Sec. IV it is shown that the generalized bracket, in the form introduced in Ref. [18], subsumes the Dirac formalism for constrained systems; in Sec. V, using a specific choice of the Dirac bracket, phase space equations of motion for systems with holonomic constraints are written down and their numerical integration is critically discussed; in Sec. VI the distribution function for such systems, which is defined in terms of the invariant measure, is derived; in Sec. VII a computable form of the linear response of a constrained system is given. A simple example is also worked out in detail to show that correction terms, arising in the response function, are zero for systems with holonomic constraints. The last section is devoted to conclusions.

II. GENERALIZED EQUATIONS OF MOTION

Let $\mathbf{x}=(\mathbf{q},\mathbf{p})$ be the point in a phase space of dimension $2N$. Consider the antisymmetric matrix field

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$$\mathcal{B}_{ij}(\mathbf{x}) = -\mathcal{B}_{ji}(\mathbf{x}), \quad i,j=1,\ldots,2N, \tag{1}$$

by means of which one can define the generalized algebraic bracket

$$(a,b) = \sum_{i,j=1}^{2N} \frac{\partial a}{\partial x_i} \mathcal{B}_{ij}(\mathbf{x}) \frac{\partial b}{\partial x_j}, \tag{2}$$

where $a = a(\mathbf{x})$ and $b = b(\mathbf{x})$ are generic phase space functions. Equation (2) reduces to the standard Poisson bracket [35] when one adopts the constant antisymmetric matrix

$$\mathcal{B}_{ij} = \mathcal{B}^c_{ij} = \begin{bmatrix} \mathbf{0} & \mathbf{1} \\ -\mathbf{1} & \mathbf{0} \end{bmatrix}. \tag{3}$$

The generalized bracket in Eq. (2) obeys the following properties:

$$(a,b) = -(b,a), \tag{4}$$

$$(a,bc) = (a,b)c + b(a,c), \tag{5}$$

$$(k,a) = 0, \tag{6}$$

where k is a constant and a, b, and c are phase space functions. In general the Jacobi relation will not be satisfied:

$$[a,(b,c)] + [c,(a,b)] + [b,(c,a)] \neq 0. \tag{7}$$

When Eq. (7) holds, the generalized bracket does not define a Lie algebra in phase space.

Considering the phase space expression of the energy $\mathcal{H}(\mathbf{x})$, generalized equations of motion can be written in the form [17,18]

$$\dot{x}_i = (x_i, \mathcal{H}) = \sum_{j=1}^{2N} \mathcal{B}_{ij} \frac{\partial \mathcal{H}}{\partial x_j}, \quad i=1,\ldots,2N. \tag{8}$$

The time variation of any other phase space function $a = a(\mathbf{x})$ is then given by

$$\dot{a} = (a,\mathcal{H}) = \sum_{i=1}^{2N} \dot{x}_i \frac{\partial a}{\partial x_i} = iLa, \tag{9}$$

where the last equality defines the Liouville operator iL. Flows defined by Eq. (8) usually have nonzero phase space compressibility:

$$\kappa = \sum_{i=1}^{2N} \frac{\partial \dot{x}_i}{\partial x_i} = \sum_{ij}^{2N} \frac{\partial \mathcal{B}_{ij}}{\partial x_i} \frac{\partial \mathcal{H}}{\partial x_j}. \tag{10}$$

It follows immediately from the antisymmetric property of the bracket, Eq. (4), that the energy $\mathcal{H}$ is conserved [17] by the equations of motion (8). In the following $\mathcal{H}$ will be simply referred to as the Hamiltonian, even if the term is not mathematically precise.

In Refs. [17,18] it has been shown that Nosé-Hoover [19,20], Nosé-Hoover chains [21], and Andersen-Nosé [22,23] equations of motion and their associated statistical mechanics can be easily addressed within the above approach.

III. STATISTICAL MECHANICS

Considering the distribution function ρ, weighting the initial conditions, ensemble averages [30,36] in the Heisenberg picture of statistical mechanics are written as

$$\langle a \rangle(t) = \int dx \rho(x(0)) a(x(t)). \tag{11}$$

One can go to the Schrödinger picture [18,36]

$$\langle a \rangle(t) = \int dx \rho(x(t)) a(x), \tag{12}$$

where instead a is fixed in time and ρ obeys the time-independent Liouville equation

$$\frac{\partial \rho}{\partial t} = -(iL + \kappa)\rho = \sum_{i=1}^{2N} \frac{\partial}{\partial x_i}(\dot{x}_i \rho). \tag{13}$$

In an equilibrium ensemble one has

$$\partial \rho_{\mathrm{e}} / \partial t = -(iL + \kappa)\rho_{\mathrm{e}} = 0. \tag{14}$$

Tuckerman *et al.* [24–26] provided an alternative formulation of non-Hamiltonian statistical mechanics which has the merit to put the invariant measure into evidence. In their approach the equilibrium distribution function is written as the product of a true probability density f and a metric factor $\sqrt{g}$,

$$\rho_{\mathrm{e}}(x) = \sqrt{g} f_e(x) = e^{-w(x)} f_e(x), \tag{15}$$

where $w(x)$ is the primitive function of the compressibility such that $d/dt\, w(x) = \kappa(x)$. Consequently, the form of Liouville equation, in Eqs. (13) and (14), should change. However, equivalent results [18,30] can be obtained using Eqs. (13) and (14). In this case, one must check at the end of the derivation that, indeed, the invariant measure can be obtained.

The stationary solution [18,24–26,30] of Eq. (14) is

$$\rho_{\mathrm{e}} = \sum_{\alpha=1}^{M} \delta(\mathcal{K}_\alpha) e^{-w(x)}, \tag{16}$$

where $\mathcal{K}_\alpha$, $\alpha = 1,\ldots,M$ are the relevant constants of motion which permit to specify the thermodynamical ensemble [36]. In fact, it is worth to mention that one cannot include all mechanical constants of motion. To understand why, one can consider an integrable system. In this case the trajectory in phase space, which exists by definition, could be described by $2N-1$ constant hypersurfaces. Only a few of these constants of motion are suited to define a thermodynamical ensemble. They are those related to symmetries of the system that survive the process of averaging over initial conditions [36]. As discussed by Jaynes [37], they specify the allowed physical states of the system.

It has been shown by Tuckerman *et al.* that the primitive function w always exists [24–26] for integrable equilibrium flows [30]. In fact, defining the Jacobian $J_t = |\partial x(t)/\partial x(0)|$, one finds the equation $d/dt \ln J_t = \kappa$ which shows that the compressibility is exactly integrable. One can check by direct substitution that ρ_e, given by Eq. (16), is indeed a solution of the Liouville equation (19).

To carry out linear response theory, one considers an explicit time-dependent Liouville operator. Usually the explicit time dependence arises from a perturbed $\mathcal{H}_P(t)$. In the present generalized formalism, the explicit time dependence could also arise from the elements $\mathcal{B}_{ij}$ in Eq. (8). In the time-dependent case, the Heisenberg picture of statistical mechanics requires that

$$a(x(t)) = U(t)a(x) = \mathcal{T}\left(\exp\int_0^t iL(t')dt'\right)a(x), \quad (17)$$

where $\mathcal{T}$ is the time-ordering operator and $U(t)$ is the propagator. Within the Schrödinger picture the distribution function evolves under the adjoint propagator

$$\rho(x,t) = U^{\dagger}(t)\rho(x) = \mathcal{T}\exp\left[-\int_0^t [iL(t') + \kappa(t')]dt'\right]\rho(x). \quad (18)$$

Equation (18) is tantamount to writing the general time-dependent Liouville equation

$$\frac{\partial\rho(x,t)}{\partial t} = -[iL(t) + \kappa(t)]\rho(x,t) = \sum_{i=1}^{2N} \frac{\partial}{\partial x_i}[\dot{x}_i(t)\rho(x,t)]. \quad (19)$$

In the following, the elements $\mathcal{B}_{ij}$ will not explicitly depend on time. In this case it has been shown in Ref. [18] that if one considers the perturbed Hamiltonian $\mathcal{H}_P(t) = \mathcal{H}_0 + \mathcal{H}_I(t)$, where $\mathcal{H}_0$ governs the dynamics of the system in the absence of the external field and $\mathcal{H}_I(t) = -a(x)\mathcal{F}(t)$ is an explicitly time-dependent interaction term, then, as usual, the time-dependent Liouville equation (19) can be used to derive the linear response of the system. To this end, it is useful to introduce the phase space compressibilities

$$\kappa_0 = \sum_{i,j=1}^{2N} \frac{\partial\mathcal{B}_{ij}}{\partial x_i}\frac{\partial\mathcal{H}_0}{\partial x_j}, \quad (20)$$

$$\kappa_I(t) = \sum_{i,j=1}^{2N} \frac{\partial\mathcal{B}_{ij}}{\partial x_i}\frac{\partial\mathcal{H}_I(t)}{\partial x_j} = -\sum_{i,j=1}^{2N} \frac{\partial\mathcal{B}_{ij}}{\partial x_i}\frac{\partial a}{\partial x_j}\mathcal{F}(t)$$
$$\equiv -\kappa_a\mathcal{F}(t). \quad (21)$$

The phase space compressibility of the perturbed system is obviously given by $\kappa_P(t) = \kappa_0 + \kappa_I(t)$. One is also led to consider the Liouville operators $iL_0 = (\ldots, \mathcal{H}_0)$ and $iL_I(t) = (\ldots, \mathcal{H}_I(t))$ with $iL_P(t) = iL_0 + iL_I(t)$. Assuming as usual that in the distant past the system was in equilibrium, the perturbed distribution function to linear order is $\rho_P(t) = \rho_e + \Delta\rho_I(t)$, where the linear correction term has the form [18]

$$\Delta\rho_I(t) = \int_{\infty}^{t} d\tau \exp[-(t-\tau)(iL_0 + \kappa_0)]$$
$$\times[(\rho_e, a) + \kappa_a\rho_e]\mathcal{F}(\tau). \quad (22)$$

To derive Eq. (22) we used the fact that the compressibility κ_0 disappears from the propagator $U^{\dagger}(t) = \exp[-(L_0 + \kappa_0)(t)]$ when calculating its adjoint $U(t) = \exp[L_0(t)]$ by integration by part, as already discussed in Ref. [18].

Considering an arbitrary phase space function $b = b(x)$, its response $\overline{\Delta b}(t) = \overline{b}(t) - \langle b\rangle_e$ is given by

$$\overline{\Delta b}(t) = \int_{-\infty}^{t} d\tau\phi(\tau)\mathcal{F}(t-\tau), \quad (23)$$

where, as shown in Ref. [18], the response function $\phi(t)$ can be written in the compact form

$$\phi(t) = -\langle(b(t), a)\rangle_e. \quad (24)$$

A form of the response function, equivalent to that in Eq. (24) but more useful for numerical calculations, can be obtained by simple integration by parts:

$$\phi(t) = \int dx\, b(x(t))[(\rho_e, a) + \kappa_a\rho_e]. \quad (25)$$

Using Eq. (15), the response function in Eq. (25) can be written as

$$\phi(t) = \int dx\sqrt{g}\, b(x(t))[(f_e(x), a)$$
$$-f_e(x)(w(x), a) + \kappa_a f_e(x)]. \quad (26)$$

IV. DIRAC BRACKET FOR SYSTEM WITH CONSTRAINTS

Consider a system with Hamiltonian $\mathcal{H}_0$ and a set of phase space constraints:

$$\chi_\alpha(x) = 0, \quad \alpha = 1, \ldots, 2l. \quad (27)$$

Following Dirac [7,8], one can introduce the matrix

$$C_{\alpha\beta} = \{\chi_\alpha, \chi_\beta\} = \sum_{i,j=1}^{2N} \frac{\partial\chi_\alpha}{\partial x_i}\mathcal{B}^c_{ij}\frac{\partial\chi_\beta}{\partial x_j} \quad (28)$$

and its inverse $(\mathbf{C}^{-1})_{\alpha\beta}$, where $\alpha, \beta = 1, \ldots, 2l$. In the expressions above, involving the Poisson bracket of the constraints, and in the following ones, where the generalized bracket of the constraints will be introduced, one must follow the convention [7,8] of evaluating brackets first and then impose the constraints relations. By defining an antisymmetric matrix $\mathcal{B}^D$,

$$\mathcal{B}_{ij}^{D}(x)=\mathcal{B}_{ij}^{c}-\sum_{k,m=1}^{2N}\sum_{\alpha,\beta=1}^{2l}\mathcal{B}_{ik}^{c}\frac{\partial\chi_\alpha}{\partial x_k}(\mathbf{C}^{-1})_{\alpha\beta}\frac{\partial\chi_\beta}{\partial x_m}\mathcal{B}_{mj}^{c}, \tag{29}$$

an algebraic Dirac bracket can be introduced as

$$(a,b)_D=\sum_{i,j=1}^{2N}\frac{\partial a}{\partial x_i}\mathcal{B}_{ij}^{D}\frac{\partial b}{\partial x_j}. \tag{30}$$

Equation (30) defines the Dirac bracket establishing the phase space algebra of systems subjected to constraints [7,8]. It was originally introduced by Dirac in the alternative but equivalent form [7,8]

$$(a,b)_D=\{a,b\}-\sum_{\alpha,\beta=1}^{2l}\{a,\chi_\alpha\}(\mathbf{C}^{-1})_{\alpha\beta}\{\chi_\beta,b\}. \tag{31}$$

Dirac also proved that this bracket satisfies the properties in Eqs. (4)–(6) and the Jacobi relation [7,8], so that it defines a Lie algebra in phase space. The bracket in Eq. (30) is equivalent to the one in Eq. (31) and satisfies the Jacobi identity too.

The phase space flow can now be defined by

$$\dot{a}=(a,\mathcal{H}_0)_D. \tag{32}$$

This flow has the property of conserving the Hamiltonian and any function of the constraints. To show this, one can consider the action of the Dirac bracket on a general function $f(\chi_\sigma)$ of the constraints

$$(f(\chi_\sigma),H_0)_D=0. \tag{33}$$

Equation (33) can be proved by simply using the definition of the bracket in Eq. (31) and the definition of $\mathbf{C}$ and $\mathbf{C}^{-1}$. It shows that general functions of the constraints are left invariant, by construction, under infinitesimal contact transformations realized by means of the Dirac bracket.

V. PHASE SPACE FLOW FOR SYSTEMS WITH HOLONOMIC CONSTRAINTS

Consider a system with a number l of holonomic constraints in configuration space $\sigma_\alpha(\{r\})=0$, $\alpha=1,\ldots,l$. One would like to setup a mathematical framework in order to treat such a system using a generalized bracket in phase space. To this end, the following additional constraints must also be considered $\dot{\sigma}_\alpha(\{r,\dot{r}\})=\Sigma_{i=1}^{N}\boldsymbol{\nabla}\sigma_\alpha p_i/m_i=0$, $\alpha=1,\ldots,l$. In Ref. [15] it has been argued that, within Dirac approach, the constraints $\dot{\sigma}_\alpha$, $\alpha=1,\ldots,l$, can be considered as redundant and that Hamiltonian equations of motion arising from Dirac formalism are equivalent with Lagrangian equations of motion, derived by taking in account only the set of σ_α constraints. Nevertheless, the set of $\dot{\sigma}_\alpha$ constraints is required to establish a Hamiltonian picture of the dynamics. It is in fact easy to verify that without them the matrix $C_{\alpha\beta}$ in Eq. (28) would be identically zero and the Dirac bracket, as defined by Eq. (30) by means of Eq. (29), could not be defined.

In order to explicitly determine the Dirac bracket of Eq. (30) in this specific case, the whole set of constraints can be denoted as

$$(\chi_1,\ldots,\chi_l,\chi_{l+1},\ldots,\chi_{2l})=(\sigma_1,\ldots,\sigma_l,\dot{\sigma}_1,\ldots,\dot{\sigma}_l). \tag{34}$$

It is easy to see that the antisymmetric matrix $C_{\alpha\beta}$ has a block structure

$$\mathbf{C}=\begin{bmatrix}\mathbf{0} & \{\boldsymbol{\sigma},\dot{\boldsymbol{\sigma}}^T\}\\ -\{\boldsymbol{\sigma},\dot{\boldsymbol{\sigma}}^T\} & \{\dot{\boldsymbol{\sigma}},\dot{\boldsymbol{\sigma}}^T\}\end{bmatrix}. \tag{35}$$

To derive its explicit form, one considers

$$\{\sigma_\alpha,\sigma_\beta\}=0, \tag{36}$$

$$\{\sigma_\alpha,\dot{\sigma}_\beta\}=\sum_{i=1}^{N}\frac{1}{m_i}\boldsymbol{\nabla}_i\sigma_\alpha\boldsymbol{\nabla}_i\sigma_\beta, \tag{37}$$

and

$$\{\dot{\sigma}_\alpha,\dot{\sigma}_\beta\}=\sum_{i,k=1}^{N}\left(\frac{p_i}{m_i}\frac{1}{m_k}\nabla_{ki}^2\sigma_\alpha\boldsymbol{\nabla}_k\sigma_\beta-\frac{p_i}{m_i}\frac{1}{m_k}\boldsymbol{\nabla}_k\sigma_\alpha\nabla_{ki}^2\sigma_\beta\right)$$
$$=\Gamma_{\alpha\beta}. \tag{38}$$

Then, defining the matrix $Z_{\alpha\beta}=\Sigma_i(1/m_i)\boldsymbol{\nabla}_i\sigma_\alpha\boldsymbol{\nabla}_i\sigma_\beta$, one has

$$\{\boldsymbol{\chi},\boldsymbol{\chi}^T\}=\begin{bmatrix}0 & \mathbf{Z}\\ -\mathbf{Z} & \Gamma\end{bmatrix}. \tag{39}$$

It is not difficult to see that the inverse matrix is given by

$$\mathbf{C}^{-1}=\begin{bmatrix}\mathbf{Z}^{-1}\Gamma\mathbf{Z}^{-1} & -\mathbf{Z}^{-1}\\ \mathbf{Z}^{-1} & 0\end{bmatrix}. \tag{40}$$

The Dirac bracket generates the equations of motion for the phase space coordinates $x=(r,p)$. They are explicitly given by

$$(r_i,\mathcal{H}_0)_D=\frac{p_i}{m_i}-\sum_{\alpha=1}^{l}\frac{\partial\dot{\sigma}_\alpha}{\partial p_i}\mu_\alpha=\frac{p_i}{m_i}, \tag{41}$$

where the quantities

$$\mu_\alpha=\sum_{\beta=1}^{l}Z_{\alpha\beta}^{-1}\{\sigma_\beta,H\}=\sum_{\beta=1}^{l}Z_{\alpha\beta}^{-1}\dot{\sigma}_\beta=0 \tag{42}$$

have been defined.

Consider now the equations of motion for the momenta

$$(p_i,\mathcal{H}_0)_D=F_i-\sum_{\alpha=1}^{l}\boldsymbol{\nabla}_i\sigma_\alpha\lambda_\alpha, \tag{43}$$

where one has introduced the quantities

$$\lambda_\alpha = \sum_{\beta=1}^{l} Z^{-1}_{\alpha\beta}\{\dot{\sigma}_\beta, H\}$$
$$= \sum_{\beta=1}^{l} Z^{-1}_{\alpha\beta}\left(\sum_{k,j=1}^{N} \frac{p_l}{m_l}\frac{p_k}{m_k}\nabla^2_{kj}\sigma_\beta - \sum_{k=1}^{N}\frac{F_k \boldsymbol{\nabla}_k \sigma_\beta}{m_k}\right), \tag{44}$$

which correspond to the analytical value of the Lagrangian multipliers. As shown by Dirac [7,8] and discussed in Ref. [15], the equations of motion (41) and (43), expressed by means of the auxiliary quantities in Eqs. (42) and (44), may be derived by following an alternative route. One could start from the unconstrained Hamiltonian $\mathcal{H}_0$ and add the constraints to define the modified Hamiltonian

$$\mathcal{H}'_0 = \mathcal{H}_0 + \sum_{\alpha=1}^{l} (\lambda_\alpha \sigma_\alpha - \mu_\alpha \dot{\sigma}_\alpha). \tag{45}$$

Then one can derive the equations of motion using the Poisson bracket and $\mathcal{H}'_0$ as the generator of time translations [7,8]. To achieve this one must adopt the convention that the auxiliary quantities have to be treated as constants (Lagrangian multipliers) under the action of the Poisson bracket.

At this point, before deriving the equilibrium distribution function, it is worth making a little digression and considering the issue of numerically integrating the Eqs. (41) and (43). The problem can be attacked within the time reversible algorithms based on the Trotter factorization of the propagator [38–40]. To Eqs. (41) and (43) one can associate the partial Liouville operators

$$L_1 = \sum_{i=1}^{N} \frac{p_i}{m_i}\frac{\partial}{\partial r_i}, \tag{46}$$

$$L_2 = \sum_{i=1}^{N} F_i \frac{\partial}{\partial p_i} - \sum_{\alpha=1}^{l} \lambda_\alpha \sum_{i=1}^{N} \nabla_i \sigma_\alpha \frac{\partial}{\partial p_i}. \tag{47}$$

The propagator for a small time step Δt is

$$G(\Delta t) = \exp[(L_1 + L_2)\Delta t]$$
$$= \exp\left[L_2 \frac{\Delta t}{2}\right]\exp[L_1 \Delta t]\exp\left[L_2\frac{\Delta t}{2}\right] + O(\Delta t^3), \tag{48}$$

where in the last line a simple symmetric Trotter factorization [40,41], leading to the velocity Verlet algorithm, has been chosen. Using the resulting operators one would get the propagator

$$G'(\Delta t) = \prod_{i=1}^{N} \exp\left[\frac{\Delta t}{2}\left(F_i - \sum_{\alpha=1}^{l}\lambda_\alpha \boldsymbol{\nabla}_i \sigma_\alpha\right)\frac{\partial}{\partial p_i}\right]$$
$$\times \exp\left[\Delta t \frac{p_i}{m_i}\frac{\partial}{\partial r_i}\right]\exp\left[\frac{\Delta t}{2}\left(F_i - \sum_{\alpha=1}^{l}\lambda_\alpha \nabla_i \sigma_\alpha\right)\frac{\partial}{\partial p_i}\right]$$
$$+ O(\Delta t^3). \tag{49}$$

In Eq. (49) the Lagrange multipliers λ_α are not numbers but phase space functions whose expression is given by Eq. (44). For this reason the application of the factorized propagator in Eq. (49) to the phase space point, that would give, at least in principle, a dynamics exactly satisfying the constraints, is very difficult to calculate explicitly. Closed analytical formulas have been found only for particular cases [42–44]. Instead, if one forgets that the Lagrange multipliers are actually phase space functions and considers them as simple numbers, then the application of the propagator in Eq. (49) to the phase space point gives a time translation resulting in the well-known velocity Verlet algorithm

$$r_i(\Delta t) = r_i(0) + \frac{\Delta t}{m_i}p_i(0) + \frac{\Delta t^2}{2m_i}F_i(0)$$
$$- \frac{\Delta t^2}{2m_i}\sum_{\alpha=1}^{l}\lambda_\alpha(0)\boldsymbol{\nabla}_i\sigma_\alpha(0), \tag{50}$$

$$p_i(\Delta t) = p_i(0) + \frac{\Delta t}{2}[F_i(0) + F_i(\Delta t)]$$
$$- \frac{\Delta t}{2}\left(\sum_{\alpha=1}^{l}\lambda_\alpha(0)\boldsymbol{\nabla}_i\sigma_\alpha(0) + \lambda_\alpha(\Delta t)\boldsymbol{\nabla}_i\sigma_\alpha(\Delta t)\right). \tag{51}$$

If one now substitutes the exact expressions in Eq. (44) we obtain an algorithm that does not satisfy the constraints because of an exponential growing error. The above discussion unveils the origin of this instability by showing its relation to a too *naive* approximation to the action of the propagator in Eq. (49). Equations (50) and (51) were obtained considering λ_α as numerical parameters. Their numerical treatment must be consistent with such an assumption. As is well known, the solution has been given by SHAKE [1,45].

VI. INVARIANT MEASURE FOR SYSTEMS WITH HOLONOMIC CONSTRAINTS

From the explicit equations for phase space coordinates, one can calculate the flow compressibility in Eq. (20) and rewrite it for convenience as

$$\kappa_0 = \sum_{i=1}^{N}\left(\frac{\partial \dot{r}_i}{\partial r_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right). \tag{52}$$

From the equations of motion (41) and (43) one gets

$$\kappa_0 = -\sum_{i=1}^{N}\sum_{\alpha=1}^{l}\boldsymbol{\nabla}_i\sigma_\alpha\frac{\partial\lambda_\alpha}{\partial p_i}, \tag{53}$$

where the condition $\dot{\sigma}_\alpha = 0$ has been used. Finally, the phase space compressibility is obtained:

$$\kappa_0 = -\sum_{\alpha\beta=1}^{l} Z^{-1}_{\alpha\beta}\frac{dZ_{\alpha\beta}}{dt} = -\mathrm{Tr}(\dot{\mathbf{Z}}\cdot\mathbf{Z}^{-1}) = -\frac{d}{dt}\ln||\mathbf{Z}||. \tag{54}$$

From Eq. (57) one immediately finds that $w(x)$, the primitive function of the compressibility, is given by

$$w(x)=-\ln||\mathbf{Z}||. \tag{55}$$

The stationary solution of the Liouville equation (19), ρ_e, has the form given in Eq. (16). By realizing that the constant of motion is $\mathcal{H}_0$ and the constraints χ_α, $\alpha=1,\ldots,2l$, one can write ρ_e as

$$\rho_e=\delta(\mathcal{H}_0)\prod_{\alpha=1}^{2l}\delta(\chi_\alpha)||\mathbf{Z}||=\delta(\mathcal{H}_0)\prod_{\alpha=1}^{l}\delta(\sigma_\alpha)\delta(\dot{\sigma}_\alpha)||\mathbf{Z}||. \tag{56}$$

Equation (56) proves that also in the important case of constrained systems the invariant measure [24–26] arises from the generalized bracket, in this case the Dirac bracket, and the correct solution of the Liouville equation [18,30].

The invariant measure for constrained systems was derived in Ref. [46] using only constraints in configuration space. This choice precludes the possibility to formulate a proper bracket in phase space as instead done in the approach of Dirac [7,8] and illustrated by the present derivation. Nevertheless, the derivation given in Ref. [46] has been a useful guide for the one presented above. The identity of our results, obtained by means of a generalized bracket in phase space, with the one presented in Ref. [46], obtained considering only the constraints in configuration space, shows that the statistical mechanics of system with holonomic constraints can be formulated in both ways.

VII. LINEAR RESPONSE FOR CONSTRAINED SYSTEMS

Linear response for constrained systems can be obtained simply by substituting the expression of the equilibrium distribution function, Eq. (56), in Eq. (25). Since any function of the constraints [see Eq. (33)] is conserved under Dirac flow, one gets

$$(\rho_e,\mathcal{H}_I(\tau))_D=||\mathbf{Z}||\prod_\alpha\delta(\chi_\alpha)(\delta(\mathcal{H}_0),\mathcal{H}_I(\tau))_D, \tag{57}$$

where $(||\mathbf{Z}||,H_I(\tau))_D=0$ has been used, for $\mathbf{Z}$ it does not depend on particle momenta. So one is led to consider the action of the Dirac bracket on $\delta(\mathcal{H}_0)$:

$$\begin{aligned}(\delta(\mathcal{H}_0),\mathcal{H}_I(\tau))_D&=\frac{\partial\delta(\mathcal{H}_0)}{\partial\mathcal{H}_0}(\mathcal{H}_0,\mathcal{H}_I(\tau))_D\\&=-\frac{\partial\delta(\mathcal{H}_0)}{\partial\mathcal{H}_0}\dot{\mathcal{H}}_I(\tau),\end{aligned} \tag{58}$$

where the equation of motion $\dot{\mathcal{H}}_I(\tau)=(H_I(\tau),H_0)_D$ has been used. Introducing the Laplace transform representation of the δ function and taking the thermodynamic limit [47] one can show that

$$(\delta(\mathcal{H}_0),\mathcal{H}_I(\tau))_D=+\beta\delta(\mathcal{H}_0)\dot{\mathcal{H}}_I(\tau). \tag{59}$$

Finally, collecting the results, one obtains the linear response formula for a constrained system

$$\overline{\Delta b}(t)=-\int_0^t d\tau\int dx\,b(t-\tau)[\beta\dot{\mathcal{H}}_I(\tau)+\kappa_I(\tau)]\rho_e. \tag{60}$$

Equation (60) automatically expresses the average using the correct invariant measure, the latter being contained in Eq. (56). The interaction compressibility $\kappa_I(\tau)$ is expressed as

$$\kappa_I(\tau)=\sum_{i,j=1}^{2N}\frac{\partial\mathcal{B}_{ij}^D(\tau)}{\partial x_i}\frac{\partial\mathcal{H}_I(\tau)}{\partial x_j}, \tag{61}$$

where $\mathcal{B}_{ij}^D$ is given in Eq. (29). The explicit expression of $\kappa_I(\tau)$ depends on the form of the interaction Hamiltonian $\mathcal{H}_I(\tau)$ and for specific problems it could be in principle complex to evaluate. A result equivalent to Eq. (60) has also been obtained by Tuckerman *et al.* [48].

In order to make the formulas explicit, one considers a perturbation of the form

$$\mathcal{H}_I(t)=-a(x)\mathcal{F}(t). \tag{62}$$

Equation (61) becomes

$$\kappa_I(t)=-\mathcal{F}(t)\sum_{i,j=1}^{2N}\frac{\partial\mathcal{B}_{ij}^D(t)}{\partial x_i}\frac{\partial a(t)}{\partial x_j}=-\mathcal{F}(t)\kappa_a^D. \tag{63}$$

Using Eqs. (62) and (63), Eq. (60) becomes

$$\overline{\Delta b}(t)=\int d\tau\mathcal{F}(t-\tau)\Phi(\tau), \tag{64}$$

where one has introduced the response function

$$\Phi_{ba}(t)=\Phi_{ba}^1(t)+\Phi_{ba}^2(t), \tag{65}$$

where

$$\Phi_{ba}^1(t)=+\beta\int dx\rho_{eq}(x)b(x(t))\dot{a}(x), \tag{66}$$

$$\Phi_{ba}^2(t)=\int dx\rho_{eq}(x)b(x(t))\kappa_a^D. \tag{67}$$

The response function in Eq. (65) is composed of the two contributions in Eqs. (66) and (67). The contribution in Eq. (66) has the same form of that arising from linear response of Hamiltonian systems. The difference is contained in the equilibrium average over the constrained ensemble. The contribution in Eq. (67) is a correction term coming from the generalized bracket. In order to calculate this correction one must work out κ_a^D. To this end it is easy to see that

$$\frac{\partial \mathcal{B}^D_{ij}}{\partial x_i} = -\sum_{k,l}\sum_{\alpha,\beta}\mathcal{B}^c_{ik}\left[\frac{\partial^2\chi_\alpha}{\partial x_i\partial x_k}(\mathbf{C}^{-1})_{\alpha\beta}\frac{\partial\chi_\beta}{\partial x_l} + \frac{\partial\chi_\alpha}{\partial x_k}\frac{\partial(\mathbf{C}^{-1})_{\alpha\beta}}{\partial x_i}\frac{\partial\chi_\beta}{\partial x_l} + \frac{\partial\chi_\alpha}{\partial x_k}(\mathbf{C}^{-1})_{\alpha\beta}\frac{\partial^2\chi_\beta}{\partial x_i\partial x_l}\right]\mathcal{B}^c_{lj}, \tag{68}$$

where

$$\frac{\partial\mathbf{C}^{-1}}{\partial x_i} = \begin{bmatrix} \mathbf{0} & -\dfrac{\partial\mathbf{Z}^{-1}}{\partial x_i} \\ \dfrac{\partial\mathbf{Z}^{-1}}{\partial x_i} & \mathbf{0}\end{bmatrix} = \begin{bmatrix} \mathbf{0} & -\mathbf{Z}^{-1}\dfrac{\partial\mathbf{Z}}{\partial x_i}\mathbf{Z}^{-1} \\ \mathbf{Z}^{-1}\dfrac{\partial\mathbf{Z}}{\partial x_i}\mathbf{Z}^{-1} & \mathbf{0}\end{bmatrix}. \tag{69}$$

Using Eqs. (71) and (72) one can determine the quantity κ^D_a, defined by Eq. (66), which enters in the correction term of the response function of constrained systems, Eq. (70), and it must be evaluated explicitly in particular cases.

Dipole in a Lennard-Jones bath

In order to illustrate the theory with a concrete example, one could consider a dipole made by two opposite charges, $\pm q$ with phase space coordinates (R_1,P_1) and (R_2,P_2), constrained at distance d but otherwise free to move within a bath of Lennard-Jones particles with coordinate (r_i,p_i), $i=1,\ldots,N$. The Hamiltonian of the system is

$$H=\sum_{I=1}^{2}\frac{\mathbf{P}_I^2}{2M}+\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m}+V(\{\mathbf{r},\mathbf{R}\}), \tag{70}$$

where M is the mass of the charges, m is the mass of the bath particles, and $V(\{r,R\})$ is the interaction potential. The constraint on the charges is

$$\chi=\begin{bmatrix}\sigma\\ \dot{\sigma}\end{bmatrix}=\begin{bmatrix}(\mathbf{R}_1-\mathbf{R}_2)^2-d^2\\ (\mathbf{R}_1-\mathbf{R}_2)\cdot(\mathbf{P}_1-\mathbf{P}_2)\end{bmatrix}=0. \tag{71}$$

Then

$$Z=\frac{8}{M}(\mathbf{R}_1-\mathbf{R}_2)^2, \tag{72}$$

and

$$\mathbf{C}^{-1}=\begin{bmatrix} 0 & -\dfrac{M}{8(\mathbf{R}_1-\mathbf{R}_2)^2} \\ \dfrac{M}{8(\mathbf{R}_1-\mathbf{R}_2)^2} & 0\end{bmatrix}. \tag{73}$$

The quantities μ and λ are given by

$$\mu=Z^{-1}\dot{\sigma}, \tag{74}$$

$$\lambda=Z^{-1}\left(\sum_{I,J=1}^{2}\frac{P_I}{M}\frac{P_J}{M}\nabla^2_{IJ}\sigma+\sum_{I=1}^{2}\frac{\boldsymbol{\nabla}_I V\boldsymbol{\nabla}_I\sigma}{M}\right). \tag{75}$$

The equations of motion for the charged particles are

$$\dot{R}_I=\frac{P_I}{M}-\mu\frac{\partial\dot{\sigma}}{\partial P_i}, \tag{76}$$

$$\dot{P}_I=-\boldsymbol{\nabla}_I V-\lambda\boldsymbol{\nabla}_I\sigma+\mu\boldsymbol{\nabla}_I\dot{\sigma}, \tag{77}$$

for $I=1,2$.

Now, the presence of an electric field $\mathcal{E}(t)$ would cause the appearance of a perturbation Hamiltonian

$$\mathcal{H}_I=-q(\mathbf{R}_1-\mathbf{R}_2)\mathcal{E}(t) \tag{78}$$

and one could consider the response of P_1 and P_2, the momenta of the charged particles, to the applied field. Using linear response theory, Eq. (66) gives the usual velocity autocorrelation function from which, by Fourier transforming, the mobility is calculated. Due to the constraints one must also calculate the correction term in Eq. (67).

To calculate this term it is useful to fix some conventions to represent the generalized bracket of the systems. The whole phase space has dimension $D=3\times2(N+2)$ and consequently the matrices $\mathcal{B}^D$ and $\mathcal{B}^c$ have dimension $D\times D$. Anyway, only the charged particles appear in the constraints and so only the corresponding degrees of freedom appear in κ^D_a. For this reason, one can just work with the pertinent block matrix of dimensions $D_B\times D_B$ with $D_B=3\times4$. In order to simplify the notation the block matrices will be written with the same symbols of the complete ones. So, considering only the degrees of freedom of the dipole, the following order for the phase space point can be chosen:

$$\mathbf{X}=\begin{bmatrix}\mathbf{X}_1\\ \mathbf{X}_2\\ \mathbf{X}_1\\ \mathbf{X}_2\end{bmatrix}=\begin{bmatrix}\mathbf{R}_1\\ \mathbf{R}_2\\ \mathbf{P}_1\\ \mathbf{P}_2\end{bmatrix}. \tag{79}$$

Consequently, the matrix $\mathcal{B}^c$ has the following symplectic structure:

$$\mathcal{B}^c=\begin{bmatrix}\mathbf{0}&\mathbf{0}&\mathbf{1}&\mathbf{0}\\ \mathbf{0}&\mathbf{0}&\mathbf{0}&\mathbf{1}\\ -\mathbf{1}&\mathbf{0}&\mathbf{0}&\mathbf{0}\\ \mathbf{0}&-\mathbf{1}&\mathbf{0}&\mathbf{0}\end{bmatrix}, \tag{80}$$

where every element is a diagonal 3×3 matrix taking into account the different Cartesian components. Then one can see that κ^D_a, appearing in the correction term in Eq. (67), can be written as the sum of two terms:

$$\kappa^D_a=q\left(\frac{\partial\mathcal{B}^D_{I1}}{\partial X_I}\frac{\partial\mathbf{R}_{12}}{\partial\mathbf{R}_1}+\frac{\partial\mathcal{B}^D_{I2}}{\partial X_I}\frac{\partial\mathbf{R}_{12}}{\partial\mathbf{R}_2}\right). \tag{81}$$

The first is

$$\frac{\partial \mathcal{B}_{I1}^D}{\partial X_I} = -\left[\frac{\partial^2\sigma}{\partial \mathbf{P}_1 \partial \mathbf{R}_1}(\mathbf{C}^{-1})_{12}\frac{\partial \dot{\sigma}}{\partial \mathbf{P}_1} + \frac{\partial \sigma}{\partial \mathbf{R}_1}\frac{\partial (\mathbf{C}^{-1})_{12}}{\partial \mathbf{P}_1}\frac{\partial \dot{\sigma}}{\partial \mathbf{P}_1} + \frac{\partial \sigma}{\partial \mathbf{R}_1}(\mathbf{C}^{-1})_{12}\frac{\partial^2 \dot{\sigma}}{\partial \mathbf{P}_1 \partial \mathbf{P}_1}\right] - \left[\frac{\partial^2\sigma}{\partial \mathbf{P}_2 \partial \mathbf{R}_2}(\mathbf{C}^{-1})_{12}\frac{\partial \dot{\sigma}}{\partial \mathbf{P}_1} + \frac{\partial \sigma}{\partial \mathbf{R}_2}\frac{\partial (\mathbf{C}^{-1})_{12}}{\partial \mathbf{P}_2}\frac{\partial \dot{\sigma}}{\partial \mathbf{P}_1} + \frac{\partial \sigma}{\partial \mathbf{R}_2}(\mathbf{C}^{-1})_{12}\frac{\partial^2 \dot{\sigma}}{\partial \mathbf{P}_2 \partial \mathbf{P}_1}\right] = 0. \tag{82}$$

The second is

$$\frac{\partial \mathcal{B}_{I2}^D}{\partial X_I} = -\left[\frac{\partial^2\sigma}{\partial \mathbf{P}_1 \partial \mathbf{R}_1}(\mathbf{C}^{-1})_{12}\frac{\partial \dot{\sigma}}{\partial \mathbf{P}_2} + \frac{\partial \sigma}{\partial \mathbf{R}_1}\frac{\partial (\mathbf{C}^{-1})_{12}}{\partial \mathbf{P}_1}\frac{\partial \dot{\sigma}}{\partial \mathbf{P}_2} + \frac{\partial \sigma}{\partial \mathbf{R}_1}(\mathbf{C}^{-1})_{12}\frac{\partial^2 \dot{\sigma}}{\partial \mathbf{P}_1 \partial \mathbf{P}_2}\right] - \left[\frac{\partial^2\sigma}{\partial \mathbf{P}_2 \partial \mathbf{R}_2}(\mathbf{C}^{-1})_{12}\frac{\partial \dot{\sigma}}{\partial \mathbf{P}_2} + \frac{\partial \sigma}{\partial \mathbf{R}_2}\frac{\partial (\mathbf{C}^{-1})_{12}}{\partial \mathbf{P}_2}\frac{\partial \dot{\sigma}}{\partial \mathbf{P}_2} + \frac{\partial \sigma}{\partial \mathbf{R}_2}(\mathbf{C}^{-1})_{12}\frac{\partial^2 \dot{\sigma}}{\partial \mathbf{P}_2 \partial \mathbf{P}_2}\right] = 0. \tag{83}$$

So, after some tedious algebra, one derives that, since $\kappa_a^D = 0$ for the specific constraints treated, the standard Hamiltonian form of linear response holds. The vanishing of the correction terms originated from the fact that σ and $\mathbf{C}$ do not depend on the momenta and $\dot{\sigma}$ has only a linear momentum dependence. Systems more complex than that specified by the Hamiltonian in Eq. (70), and with holonomic constraints other that the simple bond-type of the example, will still satisfy the above conditions and will also provide zero correction terms.

One could think of more general nonholonomic constraints, for example, with a nonlinear dependence on both coordinates and momenta, and could obtain, in principle, a nonzero correction. In this case, one would have to derive again the explicit expression of the invariant measure since the simple formulas rederived in this paper will no longer hold. Further study is required to verify if this issue could be addressed by means of the generalized bracket.

For the moment, it is worth noticing that the bracket formulation of dynamics with holonomic constraints can be easily generalized to deal with non-Hamiltonian phase space flow with a conserved energy [17,18]. To obtain a more general bracket, still having the structure specified by Eq. (30), one has just to define the phase space point x, eventually using additional variables, and substitute $\mathcal{B}^c$ with the desired $\mathcal{B}(x)$ in Eq. (29).

VIII. CONCLUSION

In this paper the constrained dynamics of classical systems in phase space has been formulated by means of the generalized bracket previously introduced in Ref. [18]. The bracket subsumes the original Dirac approach to constrained systems. The formalism is also naturally linked to Liouville operators and propagators and has made it possible to gain some insight into the problematic treatment of constraints by means of algorithms based on the Trotter decomposition of the propagator.

The equilibrium statistical mechanics and the linear response of systems with holonomic constraints have been rederived by means of the generalized bracket in phase space. In the linear response derivation, correction terms have been found to be zero for the class of constraints explicitly treated. Further study is required to address the statistical mechanics and the linear response of systems with general nonholonomic constraints.

By means of the generalized bracket, non-Hamiltonian phase space flows with a conserved energy, as those used for systems with thermostats and barostats, can be easily combined with the Dirac formulations of the constraints and the main ideas can also be extended to treat the dynamics of quantum-classical systems [34]. In conclusion, considering the ease provided in defining energy-conserving non-Hamiltonian phase space flows, controlling their statistical mechanics, and calculating eventual corrections in the linear response, it seems that the generalized bracket formalism emerges as a simple and promising tool which can unify different ideas otherwise presented in scattered form.

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