On the geometry and entropy of non-Hamiltonian phase space

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Abstract. We analyse the equilibrium statistical mechanics of canonical, non-canonical and non-Hamiltonian equations of motion, throwing light on the peculiar geometric structure of phase space. Some fundamental issues regarding time translation and phase space measure are clarified. In particular, we emphasize that a phase space measure should be defined by means of the Jacobian of the transformation between different kinds of coordinates since such a determinant is different from zero in the non-canonical case even if the phase space compressibility is null. Instead, the Jacobian determinant associated with phase space flows is unity whenever non-canonical coordinates lead to a vanishing compressibility, so its use for defining a measure may not always be correct. To better illustrate this point, we derive a mathematical condition for defining non-Hamiltonian phase space flows with zero compressibility. The Jacobian determinant associated with the time evolution in phase space is very useful for analysing time translation invariance. The proper definition of a phase space measure is particularly important when defining the entropy functional in the canonical, non-canonical, and non-Hamiltonian cases. We show how the use of relative entropies can circumvent some subtle problems that are encountered when dealing with continuous probability distributions and phase space measures. Finally, a maximum (relative) entropy principle is formulated for non-canonical and non-Hamiltonian phase space flows.

Keywords: new applications of statistical mechanics
1. Introduction

In this paper we address some general issues concerning the geometry of non-Hamiltonian phase space under the condition of thermodynamical equilibrium. In the field of classical molecular dynamics simulations, non-Hamiltonian formalisms have been developed in order to simulate numerically the effect of thermal and pressure baths on relevant subsystems by means of a finite number of degrees of freedom [1]–[4]. It is also worth mentioning that the non-Hamiltonian approach is the method of choice for path integral [5] and \textit{ab initio} path integral molecular dynamics calculations [6]. More recently, it has been shown that the theories [7, 8] needed to describe in a consistent way the coupling between quantum and classical degrees of freedom are non-Hamiltonian in their very essence [9, 10]. Despite the ever growing number of successful applications of non-Hamiltonian theories to molecular dynamics simulations, a clarification is desirable since classical non-Hamiltonian theories in phase space have been typically formulated by means of two distinct approaches. In one case, phase space is considered as a Riemann manifold, endowed with a metric tensor whose determinant is used to define the measure of the volume element [11, 12]. Within this type of approach it is not clear how to derive non-Hamiltonian equations of motion but, once these are given, their statistical mechanics is defined by introducing an invariant measure of phase space. As a matter of fact, the metric of phase space has been exclusively linked in [11, 12] to the phase space compressibility. However, there are systems that, while being non-canonical, have a non-zero Jacobian.
and a vanishing compressibility. To show this, we derive a condition in order to define non-canonical and non-Hamiltonian systems with zero compressibility. Then, we argue that the phase space measure should be defined in terms of the Jacobian pertaining to the transformation between different kinds of coordinates (for example, canonical versus non-canonical coordinates). This Jacobian should not be confused with another Jacobian determinant, that is associated with the transformation realized by the law of motion, and which arises naturally when addressing the time translation property of statistical mechanics in phase space.

Another approach to non-Hamiltonian statistical mechanics has been proposed in [13,14]. It uses generalized antisymmetric brackets to define non-Hamiltonian equations of motion. A generalized Liouville equation for distribution functions in phase space can be written in such a way that its solutions naturally provide the statistical weight of phase space. In addition, linear response theory [13,14] as well as extensions of the theory to quantum and quantum–classical mechanics [8] can be easily formulated. Such an approach has an algebraic structure whose distinctive feature is the violation of the Jacobi relation [15]–[18]. It is important to note that the failure of the Jacobi relation implies the lack of time translation invariance of the algebra [9]. This means that if two arbitrary phase space observables obey a relation expressed by means of a generalized bracket at time $t_0$, then, in general, two such observables will not satisfy the same relation at time $t \neq t_0$. This leads to consequences in the proper definition of the constants of motion (for example, the generalized bracket of two constants of motion is not necessarily a constant of motion) and in the definition of correlation functions. An example of the application of a similar philosophy to address non-Hamiltonian phase space can be found in Ezra’s work [19,20], where the elegant formalism of differential forms and exterior derivatives has been used. More recently, such an approach has been re-expressed using the antisymmetric matrix structure introduced in [13,14] in order to devise measure-preserving algorithms for the numerical integration of non-Hamiltonian equations of motion [21].

Another issue that is particularly relevant for non-Hamiltonian statistical mechanics is the covariant definition of the entropy functional. When dealing with non-canonical and non-Hamiltonian systems with zero compressibility, care must be taken because, as discussed above, the conclusion that the measure is trivial may be erroneous [11,12]. Instead, the phase space Jacobian, which is different from unity whenever non-canonical coordinates are adopted, should be used to define the correct measure of phase space and the covariant entropy functional. However, such a functional, as already discussed in [22]–[24], can be defined without any a priori knowledge of the metric factor. The key point is that relative entropies are called for when dealing with continuous probability distributions. In fact, a relative entropy functional naturally accounts for unknown metric factors. Therefore, a maximum entropy principle can be introduced for non-canonical and non-Hamiltonian dynamics.

Since the (relative) entropy production is trivially null under the condition of thermodynamical equilibrium, a comment is called for. Indeed, it is worth underlining that, while presenting results that aim at clarifying the nature of non-Hamiltonian equilibrium geometry, we also intend to set the pre-conditions to cope with the non-equilibrium case within an information theoretical perspective (for a general introduction see [25] and references contained therein). Within such a framework, it is not really important to describe the fine-grained complexity of phase space under non-equilibrium
conditions: what matters is the ability to identify the statistical constraints which allow one to perform calculations with a predictive value.

This approach is different from another approach to non-equilibrium statistical mechanics [26] which, instead, aims at describing in a complete way the fine-grained complexity of phase space out of equilibrium. This latter approach has led, in recent years, to some important achievements such as the discovery of the fractal nature of phase space in non-equilibrium steady states [27] and an analysis of some interesting statistical models such as Anasov’s systems [28]. However, these systems are different from those investigated by chemical physics (see [29] for some recent examples). However, we believe that looking at the fine-grained nature of phase space and invoking information theoretic techniques should not be considered as mutually exclusive paths of investigation.

Clarifying the above issues is not the only goal of this paper. For an easier reading of the paper, we anticipate the results we shall illustrate in the following:

(i) We derive the conditions for obtaining a class of non-Hamiltonian phase space flows with zero compressibility.

(ii) Given that the compressibility is not a critical feature of non-Hamiltonian phase space flows, we introduce a more appropriate definition of the phase space measure by means of the Jacobian of the coordinate transformation.

(iii) We show that using the Jacobian determinant $J(t, t_0)$ that is associated with the equations of motion in order to define the phase space measure can be misleading when the compressibility vanishes. We also show that this determinant is relevant for the invariance properties of the statistical mechanical averages with respect to time translation.

(iv) We introduce a maximum entropy approach for non-Hamiltonian systems.

(v) We adopt the concept of relative entropy in order to ensure covariance in phase space. As a by-product of this analysis, we prove that Ramshaw’s covariant entropy [23] is actually a relative entropy.

The paper is divided into two main sections.

Section 2 treats the peculiar geometry of phase space and its influence on dynamics and statistical mechanics. In section 2.1, the canonical Hamiltonian phase space is briefly reviewed. The geometry of canonical phase space and its statistical mechanics are shortly discussed by means of Poisson brackets. The invariance of equilibrium statistical mechanics under time translation is discussed. Section 2.2 generalizes the result of section 2.1 to non-canonical Hamiltonian phase space flows by employing non-canonical brackets. Section 2.3 shows that non-Hamiltonian statistical mechanics is not time translation invariant. Conditions for obtaining non-Hamiltonian phase space flows with zero compressibility are also derived. Appendices A and B provide examples of simple non-canonical and non-Hamiltonian dynamics with zero compressibility.

Section 3 is devoted to a discussion of the relative entropy functional, of its covariance, and of a formula for its production rate. In section 3.1 the covariant relative entropy is illustrated and is used in order to derive a ‘maximum relative entropy’ principle. Such results are extended to the non-canonical and non-Hamiltonian cases in section 3.2. A formula for the rate of production of the relative entropy is derived in section 3.3. Concluding remarks are given in section 4.

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2. Geometry of phase space

2.1. Canonical Hamiltonian phase space

Let \( x = (q, p) \) denote a point in phase space, where \( q \) and \( p \) are generalized coordinates and momenta, respectively. Let \( \mathcal{H}(x) \) be the (Hamiltonian) generalized energy function of the system. We consider, here and in the following section, only the case in which \( \mathcal{H}(x) \) is time independent. Let \( 2n \) be the dimension of phase space. Then, the \( 2n \times 2n \) antisymmetric matrix \( B_s \), or cosymplectic form [15]–[18], reads

\[
B_s = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}.
\]  

(1)

Correspondingly, the canonical Hamiltonian equations of motion are given by

\[
\dot{x}_i = \sum_{j=1}^{2n} B_{ij}^s \frac{\partial \mathcal{H}}{\partial x_j},
\]  

(2)

for \( i = 1, \ldots, 2n \). Equations (2) can be derived from a variational principle in phase space [30] applied to the action written in symplectic form:

\[
\mathcal{A} = \int dt \left[ \sum_{i,j=1}^{2n} \frac{1}{2} \dot{x}_i B_{ij}^s x_j - \mathcal{H} \right].
\]  

(3)

The compressibility of phase space

\[
\kappa = \sum_{i=1}^{2n} \frac{\partial \dot{x}_i}{\partial x_i} = \sum_{i,j=1}^{2n} \frac{\partial B_{ij}^s}{\partial x_i} \frac{\partial \mathcal{H}}{\partial x_j}
\]  

(4)

is zero because the matrix \( B_s \) is constant. Poisson brackets can be defined as

\[
\{a(x), b(x)\}_{B^s} = \sum_{i,j=1}^{2n} \frac{\partial a}{\partial x_i} B_{ij}^s \frac{\partial b}{\partial x_j},
\]  

(5)

where \( a(x) \) and \( b(x) \) are arbitrary phase space functions, so that the equations of motion follow in the form

\[
\dot{x}_i = \{x_i, \mathcal{H}\}_{B^s}.
\]  

(6)

The Jacobi relation

\[
\{a, \{b, c\}_{B^s}\}_{B^s} + \{c, \{a, b\}_{B^s}\}_{B^s} + \{b, \{c, a\}_{B^s}\}_{B^s} = 0
\]  

(7)

is satisfied as an identity in canonical coordinates:

\[
\{x_i, x_j\}_{B^s} = B_{ij}^s.
\]  

(8)

It is well known that Poisson brackets can be used to realize infinitesimal contact transformations [15]–[17]. In particular

\[
\hat{T}_q = \{\ldots, p\}_{B^s} \delta q
\]  

(9)
is the operator realizing infinitesimal translations along the \( q \) axis and
\[
\hat{T}_p = -\{\ldots, q\}B \delta p
\] (10)
is the corresponding operator along the \( p \) axis (carrying infinitesimal changes of the generalized momenta). As a matter of fact, it can be easily verified that \( \hat{T}_q a(x) = (\partial a/\partial q) \delta q \) and \( \hat{T}_p a(x) = (\partial a/\partial p) \delta p. \) It is also easy to verify that, because of the canonical relations in (8), translations along the axis of different generalized coordinates, positions and momenta, commute. This means that canonical phase space is \textit{flat} even if generalized coordinates are used and even if the Lagrangian manifold from which one builds phase space is a Riemann manifold [16].

In order to highlight the novel features which come into play in the formalism of the non-Hamiltonian case, we think it useful to sketch briefly the equilibrium statistical mechanics of Hamiltonian canonical systems in a form that can be easily generalized to the non-canonical and non-Hamiltonian cases and that, by clearly distinguishing between the Jacobian \( J(x) \) and the Jacobian determinant \( \tilde{J}(t, t_0) \), is also suited for discussing time translation invariance.

It is well known that the Liouville operator can be introduced using Poisson brackets, \( i\hat{L} = \{\ldots, \mathcal{H}\}B. \) The Liouville equation for the statistical distribution function in phase space is written as [31]
\[
\frac{\partial \rho(x)}{\partial t} = -i\hat{L}\rho(x).
\] (11)
In equation (11), the function \( \rho(x) = J^{\text{can}}f(x) \) has been introduced, where \( f(x) \) is the true distribution function in phase space and \( J^{\text{can}} = 1 \) is the Jacobian of transformations between canonical coordinates. In the canonical case, the identity \( \rho(x) = f(x) \) trivially follows; however, this notation will turn out to be convenient later. By means of the Liouville operator one can introduce the propagator \( \exp[i t \hat{L}] = \exp[i t \{\ldots, \mathcal{H}\}P] \) whose action is defined by
\[
a(x(t)) = \exp[i t \hat{L}]a(x),
\] (12)
where \( x \) without the time argument denotes its value at time zero. Statistical averages are calculated through
\[
\langle a(x) \rangle = \int dx \rho(x)a(x),
\] (13)
and correlation functions as
\[
\langle ab(t) \rangle = \int dx \rho(x)a(x) \exp[i t \hat{L}]b(x).
\] (14)
We recall that in both equations (13) and (14) the averaging over phase space coordinates is done by considering the coordinates calculated at the initial time. Indeed, the law of motion which carries \( x(0) \) into \( x(t) \) is another transformation of coordinates:
\[
dx(0) = \tilde{J}(t, 0) dx(t),
\] (15)
where the Jacobian determinant satisfies the condition
\[
\tilde{J}(t, 0) \equiv \left| \frac{\partial x(0)}{\partial x(t)} \right| = 1.
\] (16)
At equilibrium
\[ \rho_{eq}(t) = e^{-iLt} \rho_{eq}(t) = \rho_{eq} = 0, \] (17)

and
\[ \langle a(x) \rangle = \langle a(x(t)) \rangle. \] (18)

The derivation of an analogous result for the correlation functions is more subtle and will permit us to make later important distinctions from the non-Hamiltonian case. In the Hamiltonian canonical case, we get from equation (14):
\[ \langle ab(t) \rangle = \int dx \rho_{eq}(x) a(x) b(x(t)) \]
\[ = \int dx (t) \rho_{eq}(x(t)) \left[ e^{-itL} a(x(t)) \right] b(x(t)) \]
\[ = \int dx (t) \rho_{eq}(x(t)) a(x(t)) e^{iLt} b(x(t)). \] (19)

We consider the special case in which
\[ b(x(0)) = \{ c(x(0)), d(x(0)) \}_{B^*}, \] (20)

where \( c(x) \) and \( d(x) \) are two arbitrary phase space functions. It is easy to prove that, if the Jacobi relation (7) holds, then
\[ e^{itL} \{ c(x(0)), d(x(0)) \}_{B^*} = \{ c(x(t)), d(x(t)) \}_{B^*}. \] (21)

Hence, it follows that
\[ \langle a(x) \{ c(x(t)), d(x(t)) \}_{B^*} \rangle = \int dx (t) \rho_{eq}(x(t)) a(x(t)) e^{iLt} \{ c(x(t)), d(x(t)) \}_{B^*} \]
\[ = \int dx (t) \rho_{eq}(x(t)) a(x(t)) \{ c(x(2t)), d(x(2t)) \}_{B^*} \]
\[ = \langle a(x(t)) \{ c(x(2t)), d(x(2t)) \}_{B^*} \rangle. \] (22)

Equation (22) shows that, at equilibrium and in the Hamiltonian canonical case, correlation functions are invariant under time translation. We remark that the Jacobi relation (7) is necessary for deriving this result so it can be readily foreseen that in the non-Hamiltonian case, where the Jacobi relation no longer holds, this property of time correlation functions will no longer be verified.

### 2.2. Non-canonical Hamiltonian phase space

Let us consider a transformation of phase space coordinates \( z = z(x) \) such that the Jacobian
\[ J = \left| \frac{\partial x}{\partial z} \right| \neq 1. \] (23)
Coordinates \( z \) are called non-canonical. The Hamiltonian transforms as a scalar \( \mathcal{H}(x(z)) = \mathcal{H}'(z) \) and the equations of motion become \([16, 18]\)

\[
\dot{z}_m = \sum_{k=1}^{2n} B_{mk}(z) \frac{\partial \mathcal{H}'(z)}{\partial z_k},
\]

where

\[
B_{mk} = \sum_{i,j=1}^{2n} \frac{\partial z_m}{\partial x_i} B_{ij}^s \frac{\partial z_k}{\partial x_j}.
\]

Equations of motion can also be obtained by means of the variational principle \([30]\) which arises when applying the non-canonical transformation of coordinates to the symplectic expression of the action given in equation (3). One obtains the following form for the action in non-canonical coordinates \([30]\):

\[
\mathcal{A} = \int dt \left[ \frac{1}{2} \sum_{i,j,m=1}^{2n} \frac{\partial x_i}{\partial z_m} \dot{z}_m B_{ij}^s x_j(z) - \mathcal{H}'(z) \right],
\]

on which the variation is to be performed on the \( z \) coordinates in order to obtain equations (24). Poisson brackets become non-canonical brackets defined by

\[
\{ a', b' \} = \sum_{i,j=1}^{2n} \partial a'(z) \frac{\partial B_{ij}^s(z)}{\partial z_j} \frac{\partial b'(z)}{\partial z_i},
\]

where \( a'(z) = a(x(z)) \). Non-canonical equations of motion can be expressed by means of the bracket in equation (27) as \( \dot{z}_i = \{ z_i, \mathcal{H}'(z) \}_B \). With a little bit of algebra, one can verify that non-canonical brackets satisfy the Jacobi relation as an identity. The Jacobi relation leads to the following identity for \( B(z) \):

\[
S_{ijk}(z) = \sum_{l=1}^{2n} \left( B_{il} \frac{\partial B_{jk}(z)}{\partial z_l} + B_{kl} \frac{\partial B_{ij}(z)}{\partial z_l} + B_{jl} \frac{\partial B_{ik}(z)}{\partial z_l} \right) = 0.
\]

The non-canonical brackets of phase space coordinates are given by

\[
\{ z_i, z_j \}_B = B_{ij}(z).
\]

Upon identifying the phase space point as \( z \equiv (\xi, \zeta) \), one can define the operators

\[
\hat{T}_\xi = \{ \ldots, \zeta \}_B \delta \xi,
\]

\[
\hat{T}_\zeta = -\{ \ldots, \xi \}_B \delta \zeta,
\]

which realize infinitesimal translations along the axes \( \xi \) and \( \zeta \). The non-canonical bracket relations of equation (29) imply that translations along the phase space axis in general do not commute or, in other words, phase space is curved. Notice that we do not need to introduce a metric tensor. One just has to introduce parallel transport and an affine connection, which can be implicitly defined by means of the non-canonical brackets and of the infinitesimal translation operators \( \hat{T}_\xi \) and \( \hat{T}_\zeta \).
Non-canonical phase spaces are obtained by means of a non-canonical transformation of coordinates applied to canonical Hamiltonian systems. Suppose that there is a system with a non-canonical bracket satisfying the Jacobi relation or its equivalent form given in equation (28). Suppose also that $\det B \neq 0$. Then, by means of Darboux’s theorem the system can be put (at least locally) in a canonical form. One would classify such a system as Hamiltonian: following references [16,18], we think that this property follows from the validity of the Jacobi relation. In other words, if the algebra of brackets is a Lie algebra, then the phase space is Hamiltonian [18].

For non-canonical systems, statistical mechanical averages can be calculated as

$$\langle a'(z) \rangle = \int dz \rho(z) a'(z(t)), \quad (32)$$

where

$$\rho(z) = J(z) f'(z), \quad (33)$$

the Jacobian $J(z)$ being defined in equation (23). The Liouville operator is defined by means of the non-canonical bracket

$$iL' = \{ \ldots, \mathcal{H}'(z) \} B, \quad (34)$$

while time propagation is given by

$$a'(z(t)) = \exp [itL'] a'(z) = \exp [it\{ \ldots, \mathcal{H}'(z) \} B] a'(z). \quad (35)$$

In non-canonical coordinates a compressibility

$$\kappa(z) = \sum_{ij=1}^{2n} \frac{\partial B_{ij}(z)}{\partial z_i} \frac{\partial \mathcal{H}'(z)}{\partial z_j} \quad (36)$$

might, but not necessarily, be present (see appendix A for a simple example of a non-canonical system with zero compressibility). Integrating by parts equation (32), one obtains

$$\langle a'(z) \rangle = \int dz \ a'(z) \exp[-t(iL' + \kappa(z))] \rho(z). \quad (37)$$

Equation (37) implies that $\rho(z)$ obeys the non-canonical Liouville equation

$$\frac{\partial \rho(z)}{\partial t} = -(iL' + \kappa(z)) \rho(z) = \sum_{i=1}^{2n} \frac{\partial}{\partial z_i} (\dot{z}_i \rho(z)). \quad (38)$$

It is easy to see that $dM(z) = J(z) \ dz$ provides the correct invariant measure [30]:

$$dz(t) \left| \frac{\partial x(t)}{\partial z(t)} \right| = \left| \frac{\partial x(t)}{\partial z(0)} \right| \left| \frac{\partial x(0)}{\partial z(t)} \right| \left| \frac{\partial x(0)}{\partial z(0)} \right| \left| \frac{\partial x(t)}{\partial z(0)} \right| = dz(0) \left| \frac{\partial x(0)}{\partial z(0)} \right|. \quad (39)$$

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where we have used the fact that the phase space flow in the $x$ coordinates is canonical so that $\|\partial x(t)/\partial x(0)\| = 1$. The use of the Jacobian provides the correct way of defining the invariant measure because it can also be applied when there is no compressibility [30]. However, the calculation of averages, correlation functions and linear response theory does not require the invariant measure explicitly. The knowledge of $\rho(z)$ is enough for statistical mechanics even in the non-Hamiltonian case and in the presence of constraints, as shown in [8,13,14].

It is interesting to analyse the time translation invariance of non-canonical statistical mechanics. Under time evolution, the phase space volume element transforms as

$$dz(0) = \mathcal{J}(t,0) \, dz(0),$$

where the Jacobian determinant

$$\mathcal{J}(t,0) = \left| \frac{\partial z(0)}{\partial z(t)} \right|$$

is different from unity if and only if the compressibility $\kappa$ is different from zero. As the simple example developed in appendix A shows, one can also have non-canonical equations of motion with zero compressibility. However, for the sake of comparison with the papers cited in [11], we shall explicitly consider the case in which $\kappa \neq 0$ so that $\mathcal{J}(t,0) = - \int_0^t dt' \kappa(t')$. In this case and at equilibrium

$$\langle a(z(0)) \rangle = \int dz(0)\rho_{eq}(z(0))a(z(0))$$

$$= \int dz(t)\mathcal{J}(t,0)\rho_{eq}(z(0)) \left[ e^{-iLt}a(z(t)) \right].$$

(42)

The law of evolution of the Jacobian in equation (41) is

$$\frac{d}{dt} \ln \left( \mathcal{J}(t,0) \right) = -\kappa(t).$$

(43)

Now, let

$$\frac{dw(x(t))}{dt} = \kappa(x(t)).$$

(44)

From equation (43) it can be seen that the function $w$, which is the primitive function of $\kappa$, certainly exists. Then, the Jacobian determinant can be written as

$$J(t,0) = e^{-w(x(t))}e^{w(x(0))}.$$  

(45)

The equilibrium distribution function follows as

$$\rho_{eq}(z(0)) = Z^{-1}e^{-w(0)}\delta \left( \mathcal{H}(z(0)) - C \right).$$

(46)

Then, substituting equations (46) and (45) into equation (42), we obtain

$$\langle a(z(0)) \rangle = \int dz(t)e^{-w(x(t))} \delta \left( \mathcal{H}(z(0)) - C \right) \left[ e^{-iLt}a(z(t)) \right]$$

$$= \int dz(t)e^{-w(x(t))} \delta \left( \mathcal{H}(z(t)) - C \right) \left[ e^{-iLt}a(z(t)) \right].$$

(47)
where the second equality follows because the Hamiltonian is conserved under time evolution. Then, upon integrating by parts, one obtains

$$\langle a(z(0)) \rangle = \int dz(t) \rho_{eq}(t) a(z(t)) = \langle a(z(t)) \rangle.$$  \hfill (48)

Equation (48) shows that phase space averages are time translation invariant in the non-canonical statistical mechanics of systems at equilibrium. Consider now the time correlation function

$$\langle \{ b(t), c(t) \} \rangle = \int d\{ b(0), c(0) \} \rho_{eq}(0) a(0) \{ b(t), c(t) \} = \langle \{ b(2t), c(2t) \} \rangle ,$$

where the last equality arises again from the validity of the Jacobian relation (7). Equation (49) shows that, when the bracket satisfies the Jacobi relation, the equilibrium statistical mechanics is invariant under time translation. We would like to recall that an algebra expressed by brackets satisfying the Jacobi relation is a Lie algebra. Therefore, it is reasonable to consider a phase space theory observing such a property as Hamiltonian.

2.3. Non-Hamiltonian phase space

In [13, 14] it was shown how non-Hamiltonian equations of motion, brackets and statistical mechanics can be defined. One must simply keep the generalized symplectic structure of the non-canonical equations in equation (24) and of the non-canonical bracket in equation (27) and use, in place of $\mathcal{B}(z)$, an antisymmetric matrix $\tilde{\mathcal{B}}(z)$. The matrix $\tilde{\mathcal{B}}(z)$ can be chosen arbitrarily, with the only constraint of being antisymmetric so that the Hamiltonian is conserved. As a result the Jacobi relation may not be satisfied [13]. When this happens, one of the conditions of validity of the Darboux’s theorem fails so that non-Hamiltonian phase space flows cannot be put into a canonical form. The failure of the Jacobi relation implies

$$e^{iLt} \{ a(0), b(0) \} \neq \{ a(t), b(t) \} .$$  \hfill (50)

Hence, even if the non-Hamiltonian theory has a vanishing compressibility, the equilibrium statistical mechanics is not time translation invariant. To show this, we note that

$$\langle \{ a(0), b(0) \} \rangle = \int d\tilde{z}(0) \tilde{\rho}_{eq}(0) \{ a(0), b(0) \} = \int d\tilde{z}(t) \tilde{\rho}_{eq}(t) \{ a(t), b(t) \}$$

because of equation (50).

We consider the lack of time translation invariance to be the crucial feature of non-Hamiltonian statistical mechanics.

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2.3.1. Non-Hamiltonian equations of motion with no phase space compressibility. It is easy to realize that there are non-Hamiltonian phase space flows (i.e., flows defined by brackets which do not satisfy the Jacobi relation) with zero compressibility. We refer the reader to appendix B for a trivial example. In order to show how this is possible, we consider a particular subset of non-Hamiltonian phase space flows, viz., those flows that can be derived by means of a non-integrable scaling of time. Interestingly, it was Nosé who originally considered this type of flow when he introduced his celebrated thermostat [2,4]. Nosé started with a canonical Hamiltonian system and then performed a non-canonical transformation, followed by a non-integrable scaling of time. Accordingly, we consider the non-integrable scaling of time
\[ dt = \Phi(z) \, d\tau, \] (52)
where \( \tau \) is an auxiliary time variable. Such a scaling of \( dt \) is clearly non-integrable because, due to the dependence of \( dt \) on phase space coordinates, the integral \( \int dt \) depends on the path in phase space. If we apply this scaling to equation (24), we obtain the following non-Hamiltonian equations:
\[ \frac{dz_i}{d\tau} = \sum_{j=1}^{2n} \Phi(z) B_{ij}(z) \frac{\partial H'(z)}{\partial z_j} \]
\[ = \sum_{j=1}^{2n} \tilde{B}_{ij}(z) \frac{\partial H'(z)}{\partial z_j}. \] (53)
Using the antisymmetric matrix \( \tilde{B} \) as defined in equation (53), one can introduce a non-Hamiltonian bracket
\[ \{ a', b' \}_{\tilde{B}} = \sum_{i,j=1}^{2n} \frac{\partial a'}{\partial z_i} \tilde{B}_{ij}(z) \frac{\partial b'}{\partial z_j}. \] (54)
This bracket does not satisfy the Jacobi relation so that the equations of motion (53) are non-Hamiltonian. In this case, there is a non-vanishing tensor associated with the Jacobi relation:
\[ \tilde{S}_{ijk} = \sum_{l=1}^{2n} \left( \tilde{B}_{il}(z) \frac{\partial \tilde{B}_{jk}(z)}{\partial z_l} + \tilde{B}_{kl}(z) \frac{\partial \tilde{B}_{ij}(z)}{\partial z_l} + \tilde{B}_{jl}(z) \frac{\partial \tilde{B}_{ki}(z)}{\partial z_l} \right) \neq 0. \] (55)
The compressibility of the non-Hamiltonian equations (53) is given by
\[ \tilde{\kappa}(z) = \sum_{i=1}^{2n} \frac{\partial (dz_i / d\tau)}{\partial z_i} = \sum_{i,j=1}^{2n} \frac{\partial \tilde{B}_{ij}}{\partial z_i} \frac{\partial H'(z)}{\partial z_j} \]
\[ = \sum_{i=1}^{2n} \frac{\partial \Phi(z)}{\partial z_i} \frac{dz_i}{dt} + \Phi(z) \kappa(z), \] (56)
where \( \frac{dz_i}{dt} \) and \( \kappa \) are given by the non-canonical equations of motion prior to the non-integrable time scaling. It is evident that whenever one chooses \( \Phi(z) \) in such a way that
\[ \sum_{i=1}^{2n} \frac{\partial \ln \Phi(z)}{\partial z_i} \frac{dz_i}{dt} = -\kappa(z), \] (57)
non-Hamiltonian flows have vanishing compressibility (see the trivial example given in appendix B). Correspondingly, when the scaling is chosen according to equation (57), the distribution function will obey a non-Hamiltonian equation without a compressibility:

$$\frac{\partial \tilde{\rho}(z)}{\partial \tau} = -\{\tilde{\rho}, \mathcal{H}(z)\}_B = -i\tilde{L}\tilde{\rho}(z).$$  \hspace{1cm} (58)

3. Relative entropy

3.1. The Hamiltonian case

As is well known, the definition of the entropy functional for systems with continuous probability distribution needs special care. We review, for the reader’s convenience, some relevant definitions which hold for the Hamiltonian case and which we plan to generalize to non-Hamiltonian systems in the following sections.

In order to be rigorous, one first assumes that phase space can be divided into small cells of volume $\Delta^{(i)}$ so that the coordinates in the $i$th cell are denoted as $x^{(i)}$. In this way, phase space is effectively discretized and so is the distribution function: $\rho(x^{(i)}) \equiv \rho^{(i)}$. The absolute information entropy can be defined as [24,32]

$$S[\rho] = -k_B \sum_i \rho^{(i)} \ln \rho^{(i)},$$  \hspace{1cm} (59)

where $k_B$ is Boltzmann’s constant. The continuous limit

$$S[\rho] = \lim_{\Delta^{(i)} \to 0} \left( -k_B \sum_i \rho^{(i)} \ln \rho^{(i)} \right),$$  \hspace{1cm} (60)

diverges. Upon subtracting the divergent contribution, $-k \ln \Delta^{(i)}$, one obtains the finite expression

$$S[\rho] = -k_B \int dx \rho(x) \ln \rho(x).$$  \hspace{1cm} (61)

However, as discussed in [22]–[24], the definition given in equation (61) is not acceptable because it is not coordinate independent.

When studying continuous probability distributions, one should use the relative entropy, which is a measure of the information [24] relative to a state of ignorance (represented by a given distribution function). If one denotes this latter distribution by $\mu(x)$, the relative entropy reads

$$S_{\text{rel}}[\rho] = -k_B \int dx \rho(x) \ln \left( \frac{\rho(x)}{\mu(x)} \right).$$  \hspace{1cm} (62)

For canonical Hamiltonian systems, a convenient distribution function with respect to which one can define the relative entropy is given by the distribution representing the state of absolute ignorance, i.e., the uniform distribution. Then, one can set $\mu(x) = 1$, so that, in practice, $S_{\text{rel}}[\rho]$ in equation (62) coincides with the absolute entropy $S[\rho]$ in equation (61). However, it must be realized that a uniform distribution in canonical coordinates does not necessarily transform into another uniform distribution if more general coordinates (for example non-canonical) are used. Instead, the integral in equation (62) is well defined and
its value does not depend on a specific choice of coordinates. For example, considering the transformation $x \rightarrow y$, one has

$$
\int dx \, \rho(x) \ln \left( \frac{\rho(x)}{\mu(x)} \right) = \int dy' \, \rho'(y) \ln \left( \frac{\rho'(y)}{\mu'(y)} \right),
$$

where $dx \, \rho(x) = dy' \, \rho'(y)$ and $dx \, \mu(x) = dy' \, \mu'(y)$.

The relative entropy $S_{\text{rel}}[\rho]$ in equation (62) is a measure of missing information and can be used as the starting point of a maximum entropy principle in order to obtain the form of the least biased or maximum non-committal distribution function $\rho(x)$. To this end, upon considering the two statistical constraints $\langle H \rangle = E$ and $\int dx \, \rho(x) = 1$, one is led to consider the quantity

$$
I = S_{\text{rel}}[\rho] + \lambda (E - \langle H \rangle) + \gamma \left( 1 - \int dx \, \rho(x) \right),
$$

(64)

where two Lagrangian multipliers ($\lambda$ and $\gamma$) have been introduced. Upon maximizing $I$ with respect to $\rho(x)$, the following expression for $\rho(x)$ is easily recovered:

$$
\rho(x) = Z^{-1} \mu(x) \exp \left[ -\frac{\lambda}{k_B} H(x) \right],
$$

(65)

where $Z = \int dx \, \mu(x) \exp[-(\lambda/k_B)H(x)]$. Equation (65) generalizes the standard maximum entropy principle [32] to the case of the relative entropy of continuous probability distributions. In the canonical Hamiltonian case, which has been treated in this section, $\mu(x)$ is trivially the uniform distribution. However, for non-canonical and non-Hamiltonian phase space $\mu(x)$ plays a fundamental role.

3.2. Non-canonical and non-Hamiltonian relative entropy

In the non-canonical and non-Hamiltonian case a Jacobian enters the definition of the phase space volume element. Accordingly, one should write a coordinate-independent entropy functional as

$$
S_J = -k_B \int dz \, J(z) f'(z) \ln f'(z)
$$

$$
= -k_B \int dz \, \rho(z) \ln \left( \frac{\rho(z)}{J(z)} \right),
$$

(66)

This expression is recovered starting from the relative entropy. An intrinsic (coordinate-free) form of equation (66) has been given in [20]. In order to see this, one just needs to transform equation (62) into non-canonical coordinates:

$$
\mu(x) \, dx = 1 \cdot dx = J(z) \, dz
$$

$$
f(x) \, dx = f'(z) \, J(z) \, dz = \rho(z) \, dz
$$

(67)

(68)

so that equation (66) naturally follows. If the Jacobian $J(z)$ is not known, one can use any other distribution function with respect to which the entropy is calculated, i.e., $m(x) \, dx = m'(z) \, J(z) \, dz$. Let us define $\mu(z) = m'(z) \, J(z)$, in analogy with $\rho(z) = f'(z) \, J(z)$. One can think of $\mu(z)$ as the solution of a Liouville equation with
different interactions. For example, if \( iL' = iL_0' + iL'_1 \), one may define \( \mu(z) \) as the solution of the equation

\[
\frac{\partial \mu(z)}{\partial t} = -(iL_0' + \kappa_0)\mu(z),
\]  

(69)

with \( \kappa = \kappa_0 + \kappa_1 \). The entropy determined by the additional interactions, represented by \( iL'_1 \), with respect to the state where the term \( iL'_1 \) is absent, is given by

\[
S_{\text{rel}}[\rho|\mu] = -k_B \int dz \rho(z) \ln \left( \frac{\rho(z)}{\mu(z)} \right).
\]  

(70)

Equation (70), with the correct interpretation of the distribution function \( \mu(z) \), provides a coordinate-invariant definition of the relative entropy which does not require the explicit knowledge of the metric as well as of the Jacobian. The maximum entropy principle, as written in the previous section for the canonical case, also applies without major changes to the non-canonical and non-Hamiltonian dynamics. The functional to be maximized is

\[
I = S_{\text{rel}}[\rho|\mu] + \lambda \langle E - \langle \mathcal{H}'(z) \rangle \rangle + \gamma \left( 1 - \int dz \rho(z) \right),
\]  

which provides, by setting \( \delta I / \delta \rho(z) = 0 \), the generalized canonical distribution in non-canonical coordinates

\[
\rho(z) = Z_\mu^{-1} \mu(z) \exp \left[ -\frac{\lambda}{k_B} \mathcal{H}'(z) \right].
\]  

(71)

The quantity \( Z_\mu = \int d\mu(z) \exp[-(\lambda/k_B)\mathcal{H}'(z)] \) is a weighted partition function.

### 3.3. Relative entropy production

In order to simplify the notation, we rewrite the Liouville equation as

\[
\frac{\partial \rho(x, t)}{\partial t} = -\nabla \cdot (\rho \dot{x}),
\]  

(72)

where we have introduced an obvious vectorial notation (to avoid indices) and \( \nabla = \partial / \partial x \) is the operator of differentiation with respect to phase space coordinates. From the relative entropy functional

\[
S = -k_B \int dx \rho \ln (\gamma^{-1} \rho),
\]  

(73)

the entropy production follows as

\[
\dot{S} = -k_B \int dx \left[ -\nabla \cdot (\rho \dot{x}) \ln (\gamma^{-1} \rho) + \gamma \left( \gamma^{-1} \partial_t \rho - \rho \gamma^{-2} \partial_t \gamma \right) \right].
\]  

(74)

The term \( \int dx \partial_t \rho \) vanishes because of the normalization condition on \( \rho \). Hence

\[
\dot{S} = -k_B \int dx \left[ \rho \dot{x} \cdot \nabla \ln (\gamma^{-1} \rho) - \rho \gamma^{-1} \partial_t \gamma \right].
\]  

(75)

The entropy production can then be put in the form

\[
\dot{S} = k_B (\gamma^{-1} \partial_t \gamma) - k_B \int dx \rho \dot{x} \cdot \left( \frac{\nabla \rho}{\rho} - \frac{\nabla \gamma}{\gamma} \right).
\]  

(76)

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We can show that equation (76) coincides with the formula of the covariant entropy production formerly given by Ramshaw [23] when $\gamma = \rho f^{-1}$. To this end, upon noting that

$$\rho^{-1} \nabla \rho = f^{-1} \nabla f + \gamma^{-1} \nabla \gamma$$

we obtain

$$\int d\rho \dot{x} \cdot \left[ \frac{\nabla \rho}{\rho} - \frac{\nabla \gamma}{\gamma} \right] = - \int d\rho \gamma^{-1} \nabla \cdot (\gamma \dot{x}) \cdot.$$ (78)

In the general case, we obtain from equation (76)

$$\dot{S} = k_B \left\langle \frac{1}{\gamma} \left( \frac{\partial \gamma}{\partial t} + \dot{x} \cdot \nabla \gamma \right) \right\rangle + k_B \langle \kappa \rangle,$$ (79)

and upon noting that

$$\langle \kappa \rangle = \int d\rho \frac{1}{\gamma} (\gamma \nabla \cdot \dot{x}) \cdot,$$ (80)

the relative entropy production can be written as

$$\dot{S} = k_B \langle \omega(x,t) \rangle,$$ (81)

where

$$\omega(x,t) = \frac{1}{\gamma} \left[ \frac{\partial \gamma}{\partial t} + \nabla \cdot (\gamma \dot{x}) \right].$$ (82)

Equation (81) is identical to the covariant entropy production given by Ramshaw [23]. Ezra [20] has also provided a coordinate-free expression of equation (81). Such comparisons are presented to validate our information theoretical approach to non-Hamiltonian systems at equilibrium. When $\omega = 0$, i.e., if $\gamma$ is a solution of the Liouville equation, then $\dot{S} = 0$. It is also clear that in an equilibrium ensemble ($\partial_t \rho = 0$, $\partial_t f = 0$, $\partial_t \gamma = 0$) the production of (relative) entropy is trivially null.

4. Conclusions

The geometry of phase space is peculiar. Antisymmetric brackets, which define a Lie algebra (in the canonical and non-canonical cases) or a non-Lie algebra (in the non-Hamiltonian case), can be used to connect, by means of infinitesimal ‘contact’ transformations, nearby points over the manifold. A distinctive feature of non-Hamiltonian equilibrium statistical mechanics is the lack of time translation invariance. This is mathematically represented by the failure of the Jacobi relation. As a matter of fact, whenever a bracket satisfies the Jacobi relation, the equilibrium statistical mechanics is time translation invariant and the bracket realizes a Lie algebra. We surmise that such theories should be classified as Hamiltonian.

We argue that a non-vanishing phase space compressibility is not a signature of non-canonical or non-Hamiltonian dynamics. There are cases (and it is worth noting that Andersen’s constant pressure dynamics [1] is one of these) where the compressibility is zero but the Jacobian is not unity and the dynamics is non-canonical (or non-Hamiltonian).
In particular, we have derived a condition for having a vanishing compressibility in a restricted class of non-Hamiltonian phase space flows (those flows which are obtained by means of non-canonical transformations of coordinates followed by a non-integrable scaling of time \([2, 4]\)). In such cases, it is obvious that the measure of phase space cannot be derived from the phase space compressibility. Instead, one should use the Jacobian of the transformation between different kinds of phase space coordinates. However, it is not necessary to know explicitly such a Jacobian for setting up a statistical mechanical theory. In fact, the distribution function and the Liouville operators are sufficient to this end.

We remark how, for continuous probability distributions, one should use the relative entropy functional. The definition of the relative entropy is coordinate independent and, measuring the state of ignorance relative to another given distribution does not require the explicit knowledge of the Jacobian. A maximum entropy principle, which applies to the relative entropy, has been formulated in the canonical, non-canonical and non-Hamiltonian cases. Such a maximum entropy principle may turn out to be relevant for applications in the non-Hamiltonian dynamics of non-equilibrium thermodynamical ensembles.

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**Appendix A. A non-canonical system with zero compressibility**

Consider the following simple Hamiltonian:

\[ H = \frac{p_1^2}{2} + \frac{p_2^2}{2} + \frac{1}{2}(q_1 - q_2)^2, \]  

(A.1)

whose canonical equations of motion can be easily written down. Consider, instead, the following non-canonical transformation of coordinates: \( x = (q_1, q_2, p_1, p_2) \rightarrow z = (\xi_1, \xi_2, \pi_1, \pi_2) \) defined by

\[ q_1 = \xi_1 \xi_2^{-1} \]  

(A.2)

\[ q_2 = \xi_2 \]  

(A.3)

\[ p_1 = \xi_2 \pi_1 \]  

(A.4)

\[ p_2 = \pi_2. \]  

(A.5)

By using this transformation of coordinates onto the canonical equation of motion, one obtains the following non-canonical equations of motion:

\[ \dot{\xi}_1 = \xi_1 \pi_2 \xi_2^{-1} + \xi_2^2 \pi_1 \]  

(A.6)

\[ \dot{\xi}_2 = \pi_2 \]  

(A.7)

\[ \pi_1 = -\pi_2 \xi_2^{-1} \pi_1 + \xi_2^{-1}(\xi_2 - \xi_1 \xi_2^{-1}) \]  

(A.8)

\[ \pi_2 = -(\xi_2 - \xi_1 \xi_2^{-1}). \]  

(A.9)
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The Hamiltonian in non-canonical coordinates is

\[ \mathcal{H}'(z) = \xi_2^2 \frac{\pi_1^2}{2} + \pi_2^2 + \frac{1}{2}(\xi_1\xi_2^{-1} - \xi_2)^2. \]  

(A.10)

One can calculate

\[ \frac{\partial \mathcal{H}'(z)}{\partial \xi_1} = \xi_2^{-1}(\xi_1\xi_2^{-1} - \xi_2) \]  

(A.11)

\[ \frac{\partial \mathcal{H}'(z)}{\partial \xi_2} = \xi_2 \pi_1^2 - (\xi_1\xi_2^{-1} - \xi_2)(\xi_1\xi_2^{-2} + 1) \]  

(A.12)

\[ \frac{\partial \mathcal{H}'(z)}{\partial \pi_1} = a\xi_2^2 \pi_1 \]  

(A.13)

\[ \frac{\partial \mathcal{H}'(z)}{\partial \pi_2} = \pi_2, \]  

(A.14)

and write the equations in matrix form:

\[
\begin{bmatrix}
\dot{\xi}_1 \\
\dot{\xi}_2 \\
\dot{\pi}_1 \\
\dot{\pi}_2
\end{bmatrix} =
\begin{bmatrix}
0 & 0 & 1 & \xi_1\xi_2^{-1} \\
0 & 0 & 0 & 1 \\
-1 & 0 & 0 & -\pi_1\xi_2^{-1} \\
-\xi_1\xi_2^{-1} & -1 & \pi_1\xi_2^{-1} & 0
\end{bmatrix}
\begin{bmatrix}
\frac{\partial \mathcal{H}'(z)}{\partial \xi_1} \\
\frac{\partial \mathcal{H}'(z)}{\partial \xi_2} \\
\frac{\partial \mathcal{H}'(z)}{\partial \pi_1} \\
\frac{\partial \mathcal{H}'(z)}{\partial \pi_2}
\end{bmatrix}. \]  

(A.15)

Equations (A.6)–(A.9) are obviously non-canonical, as is clearly seen by their matrix form given in equation (A.15), and they have zero compressibility. Hence, metric theories cannot be applied. The antisymmetric matrix appearing in equation (A.15) must be used to define the non-canonical bracket, which obviously satisfies the Jacobi relation and the Liouville equation.

**Appendix B. A non-Hamiltonian system with zero compressibility**

Let us consider the Hamiltonian of equation (A.1). We first obtain non-canonical equations of motion by considering the transformation of coordinates

\[ q_1 = \xi_2\xi_1 \]  

(B.1)

\[ q_2 = \xi_2 \]  

(B.2)

\[ p_1 = \pi_1 \]  

(B.3)

\[ p_2 = \pi_2. \]  

(B.4)

The Hamiltonian becomes

\[ \mathcal{H}' = \frac{\pi_1^2}{2} + \frac{\pi_2^2}{2} + \frac{\xi_2^2}{2}(\xi_1 - 1)^2. \]  

(B.5)
The non-canonical equations of motion are
\[ \dot{\xi}_1 = \xi_2^{-1}\pi_1 - \xi_1\xi_2^{-1}\pi_2 \]  \hspace{1cm} (B.6)
\[ \dot{\xi}_2 = \pi_2 \]  \hspace{1cm} (B.7)
\[ \dot{\pi}_1 = -\xi_2(\xi_1 - 1) \]  \hspace{1cm} (B.8)
\[ \dot{\pi}_2 = -\xi_2(1 - \xi_1). \]  \hspace{1cm} (B.9)

Such non-canonical equations have a compressibility
\[ \kappa = -\xi_2^{-1}\pi_2. \]  \hspace{1cm} (B.10)

We define the antisymmetric matrix
\[ B = \begin{bmatrix}
0 & 0 & \xi_2^{-1} & -\xi_2^{-1}\xi_1 \\
0 & 0 & 0 & 1 \\
-\xi_2^{-1} & 0 & 0 & 0 \\
\xi_2^{-1}\xi_1 & -1 & 0 & 0 \\
\end{bmatrix} \]  \hspace{1cm} (B.11)

which should be used in order to define the non-canonical bracket which satisfies the Jacobi relation. Now, if one wants to apply a non-integrable scaling of time in order to obtain a non-Hamiltonian flow with zero compressibility \( \kappa \), equation (57) can be used.

Assuming the scaling function \( \Phi = \Phi(\xi_2) \), one obtains
\[ \frac{\partial \Phi}{\partial \xi_2}\pi_2 = \xi_2^{-1}\pi_2, \]  \hspace{1cm} (B.12)

from which one readily finds \( \Phi = \xi_2 \). Hence, the antisymmetric matrix \( \tilde{B} = \Phi B \) is
\[ \tilde{B} = \begin{bmatrix}
0 & 0 & 1 & -\xi_1 \\
0 & 0 & 0 & \xi_2 \\
-1 & 0 & 0 & 0 \\
\xi_1 & -\xi_2 & 0 & 0 \\
\end{bmatrix}. \]  \hspace{1cm} (B.13)

Non-Hamiltonian equations of motion are now defined according to equation (53). Finally, it is not difficult to verify that the non-Hamiltonian bracket of equation (54), with \( \tilde{B} \) defined in equation (B.13), does not satisfy the Jacobi relation and \( \tilde{S}_{ijk} \neq 0 \). For example, it is easy to verify that \( \tilde{S}_{314} = 1 \).

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