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Geometric approach to response theory in non-Hamiltonian systems

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The theory of differential forms and time-dependent vector fields on manifolds is applied to formulate response theory for non-Hamiltonian systems. This approach is manifestly coordinate-free, and provides a transparent derivation of the response of a thermostatted system to a time-dependent perturbation.

KEY WORDS: non-Hamiltonian dynamics, response theory, applied differential forms

1. Introduction

The application of geometric methods and concepts from the theory of differentiable manifolds [1–5] to the description of classical Hamiltonian systems is now standard [1,6], and textbook treatments of classical mechanics based on the theory of symplectic manifolds are available [7–9]. Following early work (see [10–17]), there has been recent interest in the application of suitably generalized geometric methods to problems in the classical statistical mechanics of non-Hamiltonian systems [18–21].

Non-Hamiltonian dynamics are relevant when we consider the statistical mechanics of thermostatted systems [22–25]. Various thermostatting mechanisms have been introduced to remove heat supplied by nonequilibrium mechanical and thermal perturbations [22–24,26]. Phase space volume is no longer conserved, and for nonequilibrium steady states the phase space probability distribution appears to collapse onto a fractal set of lower dimensionality than in the equilibrium case [22,23,25,27].

In the present paper we apply the theory of differential forms and time-dependent vector fields on manifolds to formulate response theory for classical non-Hamiltonian systems [22,28–30]. The formalism we develop is worthwhile for several reasons. First, once preliminary definitions and results are in place, the theory avoids many of the rather cumbersome manipulations required in previous approaches [22,28–30]. Second, the manifest coordinate-independence of the formulation removes any question [21] concerning possible coordinate dependence of the results. Third, our approach to the computation of the time-dependent expectation values of observables in non-Hamiltonian

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systems is based on the fundamental concept of the pull-back. This notion, as applied to both ordinary functions and to differential (volume) forms, together with the more familiar concept of the Lie derivative, serves to unify and simplify the treatment of the transformation properties of phase functions (observables) and phase space distribution functions (densities) in the usual formalism [22,28–30]. Finally, our approach enables us to shed light on some recent controversies concerning the dynamics of non-Hamiltonian systems [31–37]; these issues are addressed elsewhere [38].

In section 2 of the present paper we present a very brief summary of the key concepts from the theory of differential forms that are necessary for our discussion of non-Hamiltonian systems. In section 3, the transport equation and associated covariant generalized Liouville equation for the phase space distribution function are derived. Section 4 illustrates the general ideas in the context of a simple system described by Nosé–Hoover dynamics [23,26]. In section 5 we consider evaluation of ensemble phase space averages in both the Heisenberg and Schrödinger pictures [22]. Response theory for a time-dependent perturbation of a non-Hamiltonian system [22] is developed in section 6, while section 7 concludes.

2. Essential preliminaries

It is not possible in the present paper to provide a self-contained account of the theory of vector fields and forms on manifolds; a number of excellent textbooks are available [1–5]. The discussion here is intended to establish our notation and to introduce some key concepts that are essential for later work. References are given to relevant sections of the book by Abraham, Marsden and Ratiu [3], which provides more material on time-dependent vector fields and forms than most other introductory texts.

2.1. Manifold and coordinates

The n-dimensional differentiable manifold of interest (phase space) will be denoted $\mathcal{M}$. (Local) coordinates are $\boldsymbol{x} = (x^1, \ldots, x^n)$. An example for $n = 2N$ is the phase space of a Hamiltonian system, with $2N$ canonical coordinates $(p_1, \ldots, p_N, q^1, \ldots, q^N)$. Such a manifold has a natural symplectic structure (2-form) preserved by the Hamiltonian flow [6]. We do not assume the existence of such Hamiltonian structure (although note that several apparently non-Hamiltonian thermostatted systems have underlying Hamiltonian structure [24,39]). Neither do we assume the existence of a natural metric on the manifold $\mathcal{M}$, so that phase space is not in general a Riemannian manifold in any natural sense. (Study of the Riemannian geometry of *configuration space* has yielded fundamental insights into the onset of global stochasticity in multidimensional Hamiltonian systems [40,41].) In the treatment of homogeneously thermostatted systems, the set of coordinates $\boldsymbol{x}$ consists of the position and momentum coordinates of the physical system augmented by a set of extra variables describing the thermostat [22–24,26].

2.2. Vectors and forms

The tangent vector $\boldsymbol{v}$ at $\boldsymbol{x} \in \mathcal{M}$ is an element of the tangent space $T_{\boldsymbol{x}}\mathcal{M}$. In terms of coordinate basis vectors $\mathbf{e}_j$, $j = 1, \ldots, n$,

$$\boldsymbol{v} = v^j \mathbf{e}_j = v^j \frac{\partial}{\partial x^j}, \tag{1}$$

where we sum over the repeated index j. A vector field on $\mathcal{M}$ is defined by giving a vector $\boldsymbol{v}(\boldsymbol{x}) \in T_{\boldsymbol{x}}\mathcal{M}$ at every point $\boldsymbol{x} \in \mathcal{M}$. We assume that $\boldsymbol{v}$ depends smoothly on $\boldsymbol{x}$.

The 1-form or co-vector $\boldsymbol{\alpha}$ is an element of the cotangent space, $\boldsymbol{\alpha} \in T^*_{\boldsymbol{x}}\mathcal{M}$, and can be written as a linear combination of basis 1-forms $\mathbf{d}x^j$,

$$\boldsymbol{\alpha} = \alpha_j(\boldsymbol{x})\,\mathbf{d}x^j, \tag{2}$$

where $\mathbf{d}x^j(\boldsymbol{v}) = v^j$, so that $\boldsymbol{\alpha}(\boldsymbol{v}) \equiv \langle \boldsymbol{\alpha}, \boldsymbol{v}\rangle = \alpha_j v^j$.

A p-form is a multilinear, fully antisymmetric tensor of order p; it produces a number (scalar) when acting on an ordered p-tuple of tangent vectors. The standard volume n-form for coordinates $\boldsymbol{x}$ is the n-fold exterior (wedge) product

$$\omega = \mathbf{d}x^1 \wedge \mathbf{d}x^2 \wedge \cdots \wedge \mathbf{d}x^n. \tag{3}$$

The number $\omega(\boldsymbol{v}_1, \boldsymbol{v}_2, \ldots, \boldsymbol{v}_n)$ is then the volume of the parallelepiped spanned by the n tangent vectors $(\boldsymbol{v}_1, \boldsymbol{v}_2, \ldots, \boldsymbol{v}_n)$ at $\boldsymbol{x}$. Other volume forms $\overline{\omega}$ may be defined by multiplying the standard volume form ω by a (smooth, nonzero) function $\sigma(\boldsymbol{x})$,

$$\overline{\omega} \equiv \sigma(\boldsymbol{x})\omega. \tag{4}$$

2.3. Evolution operator

The vector field $\boldsymbol{\xi}$ defined at every point $\boldsymbol{x} \in \mathcal{M}$ defines the dynamical equations

$$\frac{\mathrm{d}\boldsymbol{x}}{\mathrm{d}t} = \boldsymbol{\xi}. \tag{5}$$

We shall consider the most general case where the dynamical vector field is time-dependent, $\boldsymbol{\xi} = \boldsymbol{\xi}_t \equiv \boldsymbol{\xi}(\boldsymbol{x}, t)$. This case is appropriate to describe the equations of motion for a system subjected to a time-dependent external perturbation. The associated evolution operator or flow is $\phi_{t,s}$, which maps the point $\boldsymbol{x} \in \mathcal{M}$ at time s to the point $\phi_{t,s}\boldsymbol{x} \in \mathcal{M}$ at time t:

$$\phi_{t,s} : \boldsymbol{x} \mapsto \phi_{t,s}\boldsymbol{x}. \tag{6}$$

For fixed s, the $\{\phi_{t,s}\}$ are assumed to form a one-parameter family of diffeomorphisms of $\mathcal{M}$ onto itself

$$\phi_{t,s} : \mathcal{M} \to \mathcal{M}. \tag{7}$$

We have

$$\phi_{t,s}\phi_{s,r} = \phi_{t,r}, \tag{8a}$$

$$\phi_{t,s}\phi_{s,t} = \phi_{t,t} = \text{Identity}. \tag{8b}$$

For a general time-dependent vector field $\boldsymbol{\xi}_t$ the action of the evolution operator $\phi_{t,s}$ on $\boldsymbol{x}$ depends on both s and t, while for $\boldsymbol{\xi}$ a time-independent vector field, the evolution operator depends only on the time difference $t - s$:

$$\phi_{t,s} = \phi_{t+\tau,s+\tau} \equiv \phi_{t-s}. \tag{9}$$

2.4. *Induced action on vector fields*

The induced action of the flow $\phi_{t,s}$ on a vector field $\boldsymbol{v}$ is the push-forward (tangent map) $\phi_{t,s*} : \boldsymbol{v} \mapsto \phi_{t,s*}\boldsymbol{v}$, where

$$\boldsymbol{v} = v^i \frac{\partial}{\partial x^i}\bigg|_{\boldsymbol{x}} \mapsto \phi_{t,s*}\boldsymbol{v} = v^i \frac{\partial(\phi_{t,s}\boldsymbol{x})^j}{\partial x^i}\frac{\partial}{\partial x^j}\bigg|_{\phi_{t,s}\boldsymbol{x}}. \tag{10}$$

The matrix

$$M(t,s;\boldsymbol{x})_i^j \equiv \frac{\partial(\phi_{t,s}\boldsymbol{x})^j}{\partial x^i} \tag{11}$$

is the dynamical stability matrix [42].

2.5. *Induced action on functions and forms: the pull-back*

The pull-back $\phi_{t,s}^* B$ of the time-independent function $B = B(\boldsymbol{x})$ under the mapping $\phi_{t,s}$ is

$$[\phi_{t,s}^* B](\boldsymbol{x}) \equiv B\big(\phi_{t,s}(\boldsymbol{x})\big), \tag{12}$$

while the pull-back of a time-dependent function $f_t(\boldsymbol{x}) \equiv f(t,\boldsymbol{x})$ is defined similarly

$$[\phi_{t,s}^* f_t](\boldsymbol{x}) = f_t(\phi_{t,s}\boldsymbol{x}). \tag{13}$$

The pull-back is naturally defined as a function of the "initial" phase point $\boldsymbol{x}$.

The pull-back $\phi_{t,s}^*\boldsymbol{\alpha}$ of a p-form $\boldsymbol{\alpha}$ is defined by

$$\phi_{t,s}^*\boldsymbol{\alpha}|_{\boldsymbol{x}}(\boldsymbol{v}_1,\ldots,\boldsymbol{v}_p) = \boldsymbol{\alpha}|_{\phi_{t,s}\boldsymbol{x}}(\phi_{t,s*}\boldsymbol{v}_1,\ldots,\phi_{t,s*}\boldsymbol{v}_p). \tag{14}$$

Note that the form $\phi_{t,s}^*\boldsymbol{\alpha}$ acts on tangent vectors at the point $\boldsymbol{x}$, information on the form $\boldsymbol{\alpha}$ and tangent vectors $\phi_{t,s*}\boldsymbol{v}$ at the evolved point $\phi_{t,s}\boldsymbol{x}$ having been "pulled back" to the initial point $\boldsymbol{x}$.

The pull-back of the volume form ω (equation (3)), $\phi_{t,s}^*\omega$, is of particular significance in the statistical mechanics of Hamiltonian and non-Hamiltonian systems. Evaluation of $\phi_{t,s}^*\omega$ using (3) and (14) shows that

$$\phi_{t,s}^*\omega \equiv J_\omega(\phi_{t,s})\omega, \tag{15}$$

where $J_\omega(\phi_{t,s})(\boldsymbol{x}) = |\partial\phi_{t,s}\boldsymbol{x}/\partial\boldsymbol{x}|$ is the determinant of the dynamical stability matrix, that is, the Jacobian for the transformation (6). Obviously, $J_\omega(\phi_{t,t}) = 1$ for all t and $\boldsymbol{x}$. For Hamiltonian dynamics, the Jacobian is unity, and the volume form is invariant under the flow [6], $\phi^*_{t,s}\omega = \omega$; this is one statement of Liouville's theorem for Hamiltonian systems. For non-Hamiltonian systems, the value of the Jacobian determines the growth or shrinkage of the comoving volume element along the dynamical trajectory from $\boldsymbol{x}$ at time s to $\phi_{t,s}\boldsymbol{x}$ at time t [34]. The pull-back of the n-form $\overline{\omega}$ is [3, section 6.5.12]

$$\phi^*_{t,s}\overline{\omega} \equiv J_{\overline{\omega}}(\phi_{t,s})\,\overline{\omega} = \left|\frac{\partial\phi_{t,s}\boldsymbol{x}}{\partial\boldsymbol{x}}\right| \frac{\sigma(\phi_{t,s}\boldsymbol{x})}{\sigma(\boldsymbol{x})}\overline{\omega}. \tag{16}$$

For the case of a time-independent vector field $\boldsymbol{\xi}$, the result (16) shows that, if a function $\sigma(\boldsymbol{x})$ can be found such that

$$\frac{\sigma(\phi_t\boldsymbol{x})}{\sigma(\boldsymbol{x})} = \left|\frac{\partial\phi_t\boldsymbol{x}}{\partial\boldsymbol{x}}\right|^{-1} \tag{17}$$

for all $\boldsymbol{x}$ and t, then the volume form $\overline{\omega}$ is invariant under the flow ϕ_t [17,19].

2.6. Lie derivative

The Lie derivative $\mathcal{L}_{\boldsymbol{\xi}_t}$ of a function B along the vector field $\boldsymbol{\xi}$ is defined by

$$\mathcal{L}_{\boldsymbol{\xi}_t} B = \frac{\mathrm{d}}{\mathrm{d}\tau}\phi^*_{\tau,t}B\bigg|_{\tau=t}. \tag{18}$$

From the definition,

$$\mathcal{L}(t) \equiv \mathcal{L}_{\boldsymbol{\xi}_t} = \xi^j(t,\boldsymbol{x})\frac{\partial}{\partial x^j}, \tag{19}$$

so that the Lie derivative is a differential operator in the variables $\boldsymbol{x}$. In fact,

$$\mathcal{L}(t)B = \langle \mathbf{d}B, \boldsymbol{\xi}_t\rangle, \tag{20}$$

the directional derivative of B along $\boldsymbol{\xi}_t$.

Standard results on the Lie derivative are [3, section 4.2.31]

$$\frac{\mathrm{d}}{\mathrm{d}t}\phi^*_{t,s}B = \phi^*_{t,s}\big[\mathcal{L}(t)B\big] \tag{21a}$$

and [3, section 4.2.32]

$$\frac{\mathrm{d}}{\mathrm{d}t}\phi^*_{s,t}B = -\mathcal{L}(t)[\phi^*_{s,t}B]. \tag{21b}$$

Note the important difference between the right and left positions of $\mathcal{L}(t)$ in (21a) and (21b), respectively. For a time-dependent function f_t we have [3, p. 284, equation (8)]

$$\frac{\mathrm{d}}{\mathrm{d}t}\phi^*_{t,s}f_t = \phi^*_{t,s}\left[\mathcal{L}(t)f_t + \frac{\partial f_t}{\partial t}\right]. \tag{22}$$

The Lie derivative of a form $\boldsymbol{\alpha}$ is defined similarly, either via

$$\mathcal{L}(t)\boldsymbol{\alpha} = \frac{\mathrm{d}}{\mathrm{d}\tau}\phi^*_{\tau,t}\boldsymbol{\alpha}\bigg|_{\tau=t}, \tag{23}$$

or through Cartan's formula

$$\mathcal{L}(t)\boldsymbol{\alpha} = i_{\boldsymbol{\xi}_t}\,\mathbf{d}\boldsymbol{\alpha} + \mathbf{d}i_{\boldsymbol{\xi}_t}\boldsymbol{\alpha}, \tag{24}$$

where $\mathbf{d}$ is the exterior derivative [2,5] and $i_{\boldsymbol{\xi}_t}\boldsymbol{\alpha}$ is the interior product (contraction) of the form $\boldsymbol{\alpha}$ with the vector $\boldsymbol{\xi}_t$ [2,5]. Corresponding to (21) we have [3, section 5.4.4]

$$\frac{\mathrm{d}}{\mathrm{d}t}\phi^*_{t,s}\boldsymbol{\alpha} = \phi^*_{t,s}\big[\mathcal{L}(t)\boldsymbol{\alpha}\big] \tag{25a}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}\phi^*_{s,t}\boldsymbol{\alpha} = -\mathcal{L}(t)[\phi^*_{s,t}\boldsymbol{\alpha}], \tag{25b}$$

while if $\boldsymbol{\alpha}_t$ is explicitly time dependent (for example, $\boldsymbol{\alpha}_t = \alpha(t,\boldsymbol{x})_j\,\mathbf{d}x^j$), then [3, section 5.4.5]

$$\frac{\mathrm{d}}{\mathrm{d}t}\phi^*_{t,s}\boldsymbol{\alpha}_t = \phi^*_{t,s}\left[\mathcal{L}(t)\boldsymbol{\alpha}_t + \frac{\partial\boldsymbol{\alpha}_t}{\partial t}\right]. \tag{26}$$

From the definitions above, the action of the Lie derivative on the n-form ω is

$$\mathcal{L}(t)\omega = \mathrm{div}_\omega(\boldsymbol{\xi}_t)\omega, \tag{27}$$

where this equation defines the ω-divergence $\mathrm{div}_\omega(\boldsymbol{\xi}_t)$ of the vector field $\boldsymbol{\xi}_t$ [2,3]. The ω-divergence is independent of the coordinate system in which it evaluated; in terms of coordinates $\{x^j\}$, it is

$$\mathrm{div}_\omega(\boldsymbol{\xi}_t) = \frac{\partial}{\partial x^j}\big(\xi^j(t,\boldsymbol{x})\big), \tag{28}$$

while in terms of coordinates $\widetilde{\boldsymbol{x}} = \widetilde{\boldsymbol{x}}(\boldsymbol{x})$ it is

$$\mathrm{div}_\omega(\boldsymbol{\xi}_t) = \frac{1}{\gamma(\widetilde{\boldsymbol{x}})}\frac{\partial}{\partial\widetilde{x}^j}\big(\gamma(\widetilde{\boldsymbol{x}})\widetilde{\xi}^j(t,\widetilde{\boldsymbol{x}})\big), \tag{29}$$

where the transformed vector field components are

$$\widetilde{\xi}^j = \xi^i\frac{\partial\widetilde{x}^j}{\partial x^i}, \tag{30}$$

and $\gamma(\widetilde{\boldsymbol{x}})$ is the Jacobian $|\partial\boldsymbol{x}/\partial\widetilde{\boldsymbol{x}}|$. Note also that, in addition to being coordinate-independent, the definition of the ω-divergence does not depend in any way on the existence of a metric on $\mathcal{M}$.

The $\overline{\omega}$-divergence is defined similarly:

$$\mathcal{L}(t)\overline{\omega} = \mathrm{div}_{\overline{\omega}}(\boldsymbol{\xi}_t)\overline{\omega} \tag{31}$$

with

$$\operatorname{div}_{\overline{\omega}}(\boldsymbol{\xi}_t) = \frac{1}{\sigma(\boldsymbol{x})} \frac{\partial}{\partial x^j} \big(\sigma(\boldsymbol{x}) \xi^j(t, \boldsymbol{x})\big). \tag{32}$$

If the form α is invariant under the flow, $\phi_{t,s}^* \boldsymbol{\alpha} = \boldsymbol{\alpha}$, then clearly $\mathcal{L}(t)\boldsymbol{\alpha} = 0$. The condition that the n-form $\overline{\omega} = \sigma(\boldsymbol{x})\omega$ be invariant under the flow can be written as

$$\operatorname{div}_{\omega}(\sigma \boldsymbol{\xi}_t) = 0 \tag{33a}$$

or

$$\frac{\partial}{\partial x^j} \big(\sigma(\boldsymbol{x}) \xi^j(t, \boldsymbol{x})\big) = 0. \tag{33b}$$

It is important to note that the same symbol $\mathcal{L}(t)$ is used to denote the Lie derivative acting on functions, forms and vectors ($\mathcal{L}_{\boldsymbol{\xi}} \boldsymbol{v} = [\boldsymbol{\xi}, \boldsymbol{v}]$, the commutator of $\boldsymbol{\xi}$ and $\boldsymbol{v}$), so that the specific action of $\mathcal{L}$ depends on the nature of the operand.

2.7. *Phase space compressibility*

Using equations (15), (25a) and (27), we obtain the equation of motion for the Jacobian $J_\omega(\phi_{t,s})$:

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} \ln J_\omega(\phi_{t,s})(\boldsymbol{x}) &= \operatorname{div}_\omega\big(\boldsymbol{\xi}_t(\phi_{t,s}\boldsymbol{x})\big) && (34a)\\ &= \kappa_t(\phi_{t,s}\boldsymbol{x}), && (34b) \end{aligned}$$

where we have defined the phase space compressibility κ_t

$$\kappa_t(\boldsymbol{x}) \equiv \operatorname{div}_\omega\big(\boldsymbol{\xi}_t(\boldsymbol{x})\big) = \frac{\partial}{\partial x^j} \xi^j(t, \boldsymbol{x}). \tag{35}$$

For incompressible flow, such as Hamiltonian flow expressed in terms of canonical coordinates, the phase space compressibility $\kappa_t = 0$, so that the Jacobian is always unity. In the general case, equation (34) can be formally solved to yield

$$J_\omega(\phi_{t,s})(\boldsymbol{x}) = \exp\left[\int_s^t \mathrm{d}\tau\, \kappa_\tau(\phi_{\tau,s}\boldsymbol{x})\right]. \tag{36}$$

3. Time-dependent forms and the transport (continuity) equation

Let us define a time-dependent n-form ρ_t,

$$\rho_t \equiv f(t, \boldsymbol{x})\omega \equiv f_t\, \omega, \tag{37}$$

where $f(t, \boldsymbol{x})$ is the phase space distribution function for an ensemble of representative systems, so that the fraction of the ensemble contained in any n-dimensional phase space region (open set) $V \subseteq \mathcal{M}$ at time t is obtained by integrating the n-form ρ_t over the region V [3]

$$F_t(V) = \int_V \rho_t. \tag{38}$$

The normalization condition is

$$\int_{\mathcal{M}} \rho_t = 1 \tag{39}$$

for all t, where the integral extends over the whole phase space $\mathcal{M}$. The form ρ_t and/or function $f(t, \boldsymbol{x})$ are of central interest in the statistical mechanics of both Hamiltonian and non-Hamiltonian systems.

The essential physical requirement is conservation of ensemble members under time evolution $\phi_{t,s}$:

$$F_s(V) = F_t(\phi_{t,s} V) \tag{40a}$$

or

$$\int_V \rho_s = \int_{\phi_{t,s} V} \rho_t, \tag{40b}$$

where region V at time s evolves into region $\phi_{t,s} V$ at time t. A basic property of the pull-back $\phi^*_{t,s}\rho_t$ is however [3, section 7.1.2]

$$\int_V \phi^*_{t,s}\rho_t = \int_{\phi_{t,s} V} \rho_t, \tag{41}$$

so that conservation of ensemble members is equivalent to the condition

$$\phi^*_{t,s}\rho_t = \rho_s \tag{42}$$

for the form ρ_t. Differentiation of both sides of (42) with respect to t and use of (26) yields

$$\frac{\mathrm{d}}{\mathrm{d}t}\phi^*_{t,s}\rho_t = \phi^*_{t,s}\left[\frac{\partial \rho_t}{\partial t} + \mathcal{L}_{\boldsymbol{\xi}_t}\rho_t\right] = 0, \tag{43}$$

which leads to the transport equation for the n-form ρ_t [3, section 7.1B]:

$$\frac{\partial \rho_t}{\partial t} + \mathcal{L}_{\boldsymbol{\xi}_t}\rho_t = 0. \tag{44}$$

Written in terms of the distribution function f, (44) yields the generalized Liouville equation

$$\frac{\partial f}{\partial t} + \mathrm{div}_\omega(f\boldsymbol{\xi}_t) = \frac{\partial f}{\partial t} + \mathcal{L}(t)f + f\kappa_t = 0. \tag{45}$$

Equation (45) is the covariant form of the Liouville equation for non-Hamiltonian systems [14]. For Hamiltonian (incompressible) dynamics we have

$$\frac{\partial f}{\partial t} + \mathrm{div}_\omega(f\boldsymbol{\xi}_t) = \frac{\partial f}{\partial t} + \mathcal{L}(t) f = 0. \tag{46}$$

Equation (45) holds for both time-independent and time-dependent flows [14]. It is written in a manifestly coordinate-invariant fashion, and so cannot depend in any way on the particular coordinate system in which calculations are carried out [21]. The standard volume form ω of equation (3) is, of course, associated in a natural way with the particular set of coordinates $\boldsymbol{x} = (x^1, \ldots, x^n)$. Moreover, as the notation makes clear, the form of the generalized Liouville equation (45) does depend on the volume form ω with respect to which the divergence of $\boldsymbol{\xi}_t$ is evaluated. A different choice of volume form, $\overline{\omega}$, will lead to a different decomposition of the form ρ_t, $\rho_t = \bar{f}_t\overline{\omega}$. If $\overline{\omega}$ is time-independent, $\partial_t\overline{\omega} = 0$, $\bar{f}$ will satisfy the Liouville equation

$$\frac{\partial \bar{f}}{\partial t} + \mathrm{div}_{\overline{\omega}}\big(\bar{f}\boldsymbol{\xi}_t\big) = 0. \tag{47}$$

Once again, the form of (47) is coordinate-invariant. If the n-form $\overline{\omega}$ itself satisfies the transport equation,

$$\frac{\partial \overline{\omega}}{\partial t} + \mathcal{L}(t)\overline{\omega} = 0, \tag{48}$$

then the associated distribution function satisfies the Liouville equation

$$\frac{\partial \bar{f}}{\partial t} + \mathcal{L}(t)\bar{f} = 0. \tag{49}$$

This equation corresponds to incompressible propagation of $\bar{f}$ along the flow generated by $\boldsymbol{\xi}$ (see [3, section 8.2.1] and [21]).

If $\boldsymbol{\xi}$ is time-independent and the form ρ is stationary, so that $\partial_t\rho_t = 0$, $\partial_t f = 0$, the Liouville equation (45) becomes

$$\mathrm{div}_\omega(f\boldsymbol{\xi}) = \mathcal{L}f + f\kappa = 0. \tag{50}$$

Conversely, it is necessary to solve (50) for stationary f in order to obtain an invariant measure $\rho = f\omega$.

4. Example: Equilibrium Nosé–Hoover dynamics

To illustrate some of the concepts introduced above, we consider a system with a single degree of freedom coupled to a thermostat described by Nosé–Hoover dynamics [43,44]. The phase space is three-dimensional, where $\boldsymbol{x} = (q, p, \zeta)$, $\boldsymbol{\xi} = \dot{\boldsymbol{x}} = (\dot{q}, \dot{p}, \dot{\zeta})$, and the variable ζ is the coordinate associated with the thermostat. Equations of motion are [43]

$$\dot{q} = \frac{p}{m}, \tag{51a}$$

$$\dot{p} = F(q) - \alpha\zeta p, \tag{51b}$$

$$\dot{\zeta} = \left[\frac{p^2}{m} - kT\right], \tag{51c}$$

where $F(q) = -\partial\Phi(q)/\partial q$, $\Phi(q)$ is the system potential energy, α is a coupling parameter, k is Boltzmann's constant and T the temperature of the thermostat. If the Nosé–Hoover dynamics (51a) is ergodic (as it is unlikely to be for only a single degree of freedom [43–45]), then the associated invariant density in phase space corresponds to a canonical distribution for the (q, p) variables at temperature T.

The action of the time-independent Lie derivative associated with (51a) on a function $B(q, p, \zeta)$ is

$$\mathcal{L}B = \left[\dot{q}\frac{\partial}{\partial q} + \dot{p}\frac{\partial}{\partial q} + \dot{\zeta}\frac{\partial}{\partial \zeta}\right]B \tag{52a}$$

$$= \left[\frac{p}{m}\frac{\partial}{\partial q} + \big(F(q) - \alpha\zeta p\big)\frac{\partial}{\partial p} + \left(\frac{p^2}{m} - kT\right)\frac{\partial}{\partial \zeta}\right]B. \tag{52b}$$

The phase space compressibility is

$$\kappa(q, p, \zeta) = \frac{\partial\dot{q}}{\partial q} + \frac{\partial\dot{p}}{\partial p} + \frac{\partial\dot{\zeta}}{\partial\zeta} = -\alpha\zeta. \tag{53}$$

Define the (unnormalized) distribution function

$$f^{(0)} = \exp\left[-\frac{1}{kT}\left\{\frac{p^2}{2m} + \Phi(q) + \frac{\alpha\zeta^2}{2}\right\}\right] \tag{54}$$

and associated 3-form

$$\rho^{(0)} = f^{(0)}\omega = f^{(0)}\,\mathbf{d}q \wedge \mathbf{d}p \wedge \mathbf{d}\zeta. \tag{55}$$

Direct calculation shows that

$$\mathcal{L}f^{(0)} = +\alpha\zeta f^{(0)}, \tag{56}$$

so that

$$\begin{aligned}
\mathcal{L}\rho^{(0)} &= \mathcal{L}\big(f^{(0)}\omega\big)\\
&= \big(\mathcal{L}f^{(0)}\big)\omega + f^{(0)}(\mathcal{L}\omega)\\
&= \big(+\alpha\zeta f^{(0)}\big)\omega + f^{(0)}\big(\kappa(q, p, \zeta)\omega\big)\\
&= (\alpha\zeta - \alpha\zeta)\rho^{(0)}\\
&= 0.
\end{aligned} \tag{57}$$

That is, the 3-form $\rho^{(0)}$ is invariant under the flow, and the associated invariant distribution function is $f^{(0)}$ [43]. As stated above, this is a canonical distribution in the (q, p) variables.

5. Average values in Heisenberg and Schrödinger picture

The ensemble average of the time-independent phase function $B(\boldsymbol{x})$ at time t is given in the Heisenberg picture [22,28,29,46] by

$$\langle B\rangle(t) = \int_{\mathcal{M}} (\phi^*_{t,0}B)\rho_0. \tag{58}$$

That is, the ensemble average is obtained by evaluating the function B at the time evolved phase points $\phi_{t,0}\boldsymbol{x}$, with initial conditions weighted by the initial distribution function $\rho_0 = f(0,\boldsymbol{x})\omega$ at $t = 0$. We have

$$\langle B\rangle(t) = \int_{\mathcal{M}} (\phi^*_{t,0}B)\rho_0 \tag{59a}$$

$$= \int_{\mathcal{M}} (\phi^*_{t,0}B)(\phi^*_{t,0}\rho_t) \tag{59b}$$

$$= \int_{\mathcal{M}} \phi^*_{t,0}(B\rho_t) \tag{59c}$$

$$= \int_{\phi_{t,0}\mathcal{M}} B\rho_t \tag{59d}$$

$$= \int_{\mathcal{M}} B\rho_t, \tag{59e}$$

where we use the fact that $\phi_{t,0}\mathcal{M} = \mathcal{M}$. Equation (59e) is the expression for $\langle B\rangle_t$ in the Schrödinger picture, where we evaluate the average of B using the time evolved distribution $\rho_t = f(t,\boldsymbol{x})\omega$, so that

$$\langle B\rangle(t) = \int_{\mathcal{M}} (\phi^*_{t,0}B)\rho_0 = \int_{\mathcal{M}} B\rho_t. \tag{60}$$

If the form ρ is invariant,

$$\phi^*_{t,0}\rho_t = \rho_0 = \rho_t \equiv \rho, \tag{61}$$

then

$$\langle B\rangle(t) = \int_{\mathcal{M}} (\phi^*_{t,0}B)\rho_0 = \int_{\mathcal{M}} B\rho_t = \int_{\mathcal{M}} B\rho = \langle B\rangle(0), \tag{62}$$

so that all observables are stationary.

Note that the results (60) are manifestly coordinate independent; they do not depend in any way upon the particular set of coordinates used to compute f or ω. Moreover, the computed averages are also invariant with respect to the particular decomposition of the time-dependent form ρ_t:

$$\rho_t = f_t\omega = \bar{f}_t\overline{\omega}. \tag{63}$$

Differentiation of the Heisenberg expression with respect to t yields

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{M}}(\phi^*_{t,0}B)\rho_0 = \int_{\mathcal{M}}\left[\frac{\mathrm{d}}{\mathrm{d}t}(\phi^*_{t,0}B)\right]\rho_0 \tag{64a}$$

$$= \int_{\mathcal{M}}\big(\phi^*_{t,0}\big(\mathcal{L}(t)B\big)\big)\rho_0 \tag{64b}$$

$$= \int_{\mathcal{M}}\big(\phi^*_{t,0}\big(\mathcal{L}(t)B\big)\big)(\phi^*_{t,0}\rho_t) \tag{64c}$$

$$= \int_{\mathcal{M}}\phi^*_{t,0}\big(\big(\mathcal{L}(t)B\big)\rho_t\big) \tag{64d}$$

$$= \int_{\phi_{t,0}\mathcal{M}}\big(\mathcal{L}(t)B\big)\rho_t \tag{64e}$$

$$= \int_{\mathcal{M}}\big(\mathcal{L}(t)B\big)\rho_t, \tag{64f}$$

while differentiation of the Schrödinger picture expression yields

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{M}}B\rho_t = \int_{\mathcal{M}}B\frac{\partial}{\partial t}\rho_t \tag{65a}$$

$$= -\int_{\mathcal{M}}B\big(\mathcal{L}(t)\rho_t\big). \tag{65b}$$

We therefore have

$$\int_{\mathcal{M}}\big(\mathcal{L}(t)B\big)\rho_t = -\int_{\mathcal{M}}B\big(\mathcal{L}(t)\rho_t\big). \tag{66}$$

This relation is in fact true for the Lie derivative associated with any vector field $\boldsymbol{v}$, as follows from application of Stokes theorem [2,3,5]

$$\int_{\partial V}Bi_{\boldsymbol{v}}\rho = \int_V \mathbf{d}(Bi_{\boldsymbol{v}}\rho) \tag{67a}$$

$$= \int_V\big[\mathbf{d}B\wedge i_{\boldsymbol{v}}\rho + B\mathbf{d}(i_{\boldsymbol{v}}\rho)\big] \tag{67b}$$

$$= \int_V\big[\langle\mathbf{d}B,\boldsymbol{v}\rangle\rho + B(\mathrm{div}_\rho\boldsymbol{v})\rho\big] \tag{67c}$$

$$= \int_V\big[(\mathcal{L}_{\boldsymbol{v}}B)\rho + B(\mathcal{L}_{\boldsymbol{v}}\rho)\big] \tag{67d}$$

$$= 0, \tag{67e}$$

where we assume that the flux form $i_{\boldsymbol{v}}\rho$ vanishes on the boundary ∂V of region V.

The key task of response theory is then computation of the pull-back $\phi^*_{t,s}B$ and the time evolved n-form ρ_t.

5.1. Calculation of ρ_t

5.1.1. Direct solution

In order to calculate the average value $\langle B \rangle_t$ in the Schrödinger picture, it is necessary to compute the time evolved n-form $\rho_t = f(t, \boldsymbol{x})\omega$ or distribution function $f(t, \boldsymbol{x})$ in terms of $f(s, \boldsymbol{x})$, the probability density at the earlier time s. The key relation, which follows from (8b) and the condition (42), is

$$\rho_t = \phi^*_{s,t}\rho_s, \tag{68}$$

so that

$$\begin{aligned} \rho_t &= \phi^*_{s,t}(f_s\omega) && \text{(69a)}\\ &= (\phi^*_{s,t} f_s)(\phi^*_{s,t}\omega) && \text{(69b)}\\ &= (\phi^*_{s,t} f_s) J_\omega(\phi_{s,t})\omega, && \text{(69c)} \end{aligned}$$

where we have used the definition of the Jacobian J_ω. From (36) the Jacobian is

$$\begin{aligned} J_\omega(\phi_{s,t})(\boldsymbol{x}) &= \exp\left[\int_t^s \mathrm{d}\tau\, \kappa_\tau(\phi_{\tau,t}\boldsymbol{x})\right]\\ &= \exp\left[-\int_s^t \mathrm{d}\tau\, \kappa_\tau(\phi_{\tau,t}\boldsymbol{x})\right] \end{aligned} \tag{70}$$

so that we have the following relation between the distribution functions f_t and f_s

$$f(t, \boldsymbol{x}) = f(s, \phi_{s,t}\boldsymbol{x}) \exp\left[-\int_s^t \mathrm{d}\tau\, \kappa_\tau(\phi_{\tau,t}\boldsymbol{x})\right]. \tag{71}$$

To verify directly that (71) is a solution of the Liouville equation (45), differentiate with respect to t, noting

$$\begin{aligned} \frac{\partial}{\partial t} f(s, \phi_{s,t}\boldsymbol{x}) &= \frac{\partial}{\partial t}\phi^*_{s,t} f(s, \boldsymbol{x}) && \text{(72a)}\\ &= -\mathcal{L}(t)\big(\phi^*_{s,t} f(s, \boldsymbol{x})\big) && \text{(72b)}\\ &= -\mathcal{L}(t)\, f(s, \phi_{s,t}\boldsymbol{x}) && \text{(72c)} \end{aligned}$$

and

$$\begin{aligned} &\frac{\partial}{\partial t}\exp\left[-\int_s^t \mathrm{d}\tau\, \kappa_\tau(\phi_{\tau,t}\boldsymbol{x})\right] && \text{(73a)}\\ &= \left\{\frac{\partial}{\partial t}\left[-\int_s^t \mathrm{d}\tau\, \kappa_\tau(\phi_{\tau,t}\boldsymbol{x})\right]\right\} \exp\left[-\int_s^t \mathrm{d}\tau\, \kappa_\tau(\phi_{\tau,t}\boldsymbol{x})\right] && \text{(73b)}\\ &= -\big\{\kappa_t(\boldsymbol{x}) + \mathcal{L}(t)\big\} \exp\left[-\int_s^t \mathrm{d}\tau\, \kappa_\tau(\phi_{\tau,t}\boldsymbol{x})\right] && \text{(73c)} \end{aligned}$$

so that

$$\frac{\partial}{\partial t} f(t, \boldsymbol{x}) = -\big\{\kappa_t(\boldsymbol{x}) + \mathcal{L}(t)\big\} f(s, \phi_{s,t}\boldsymbol{x}) \exp\left[-\int_s^t \mathrm{d}\tau\, \kappa_\tau(\phi_{\tau,t}\boldsymbol{x})\right] \tag{74a}$$

$$= -\big\{\kappa_t(\boldsymbol{x}) + \mathcal{L}(t)\big\} f(t, \boldsymbol{x}) \tag{74b}$$

$$= -\mathrm{div}_\omega(f\boldsymbol{\xi}_t), \tag{74c}$$

which is the generalized Liouville equation (45).

For incompressible dynamics ($\kappa = 0$), (71) shows that

$$f(t, \boldsymbol{x}) = f(s, \phi_{s,t}\boldsymbol{x}). \tag{75}$$

That is, the value of the distribution function at phase point $\boldsymbol{x}$ at time t is equal to the value of f at time s evaluated at the phase point $\phi_{s,t}\boldsymbol{x}$; this phase point is mapped to $\boldsymbol{x}$ by the evolution operator $\phi_{t,s}$. The phase space distribution function is therefore a time-dependent constant of the motion [47]. For compressible systems, (45) shows that there is an additional factor involving the time history of the compressibility κ_τ along the trajectory from $\phi_{s,t}\boldsymbol{x}$ to $\boldsymbol{x}$. If the comoving volume element shrinks uniformly along the trajectory, then the value of the phase space distribution function must undergo a compensating increase in value to ensure conservation of ensemble members [34].

5.1.2. Series expansion for ρ_t

To generate a formal series expansion for the n-form ρ_t, note that

$$\rho_t = \rho_s + \int_s^t \mathrm{d}\tau\, \frac{\mathrm{d}}{\mathrm{d}\tau}\rho_\tau \tag{76a}$$

$$= \rho_s - \int_s^t \mathrm{d}\tau\, \mathcal{L}(\tau)\rho_\tau. \tag{76b}$$

By iterative substitution, we obtain in standard fashion

$$\rho_t = \phi^*_{s,t}\rho_s, \tag{77}$$

with

$$\phi^*_{s,t} = 1 + \sum_{n=1,2,\ldots} (-)^n \int_s^t \mathrm{d}\tau_1 \int_s^{\tau_1} \mathrm{d}\tau_2 \cdots \int_s^{\tau_{n-1}} \mathrm{d}\tau_n\, \mathcal{L}(\tau_1)\mathcal{L}(\tau_2)\cdots\mathcal{L}(\tau_n). \tag{78}$$

This result expresses the pull-back $\phi^*_{s,t}$ as an operator with *left*-hand-side time-ordering $\tau_1 \geqslant \tau_2 \geqslant \cdots \geqslant \tau_n$ (cf. [22,28]). If the vector field $\boldsymbol{\xi}$ is time-independent, then the time-ordered operator becomes the usual exponential and the pull-back becomes

$$\phi^*_{s,t} = \mathrm{e}^{-(t-s)\mathcal{L}}. \tag{79}$$

5.1.3. Morriss' lemma

The relation (71) can be written as

$$\rho_t = f(t, \boldsymbol{x})\omega \tag{80a}$$
$$= \phi^*_{s,t}\rho_s \tag{80b}$$
$$= \left[\phi^*_{s,t} f(s, \boldsymbol{x})\right]\left[\phi^*_{s,t}\omega\right] \tag{80c}$$
$$= \left[\phi^*_{s,t} f(s, \boldsymbol{x})\right] \exp\left[-\int_s^t \mathrm{d}\tau\, \kappa_\tau(\phi_{\tau,t}\boldsymbol{x})\right]\omega \tag{80d}$$
$$\equiv \left[\Phi^f_{t,s} f(s, \boldsymbol{x})\right]\omega, \tag{80e}$$

where it is crucial to note that by definition the operator

$$\Phi^f_{t,s} = \exp\left[-\int_s^t \mathrm{d}\tau\, \kappa_\tau(\phi_{\tau,t}\boldsymbol{x})\right]\phi^*_{s,t}, \tag{81}$$

acts upon the phase space *distribution function* $f(s, \cdot)$ only, whereas the pull-back $\phi^*_{s,t}$ acts upon the *form* ρ_s. The operator $\Phi^f_{t,s}$ incorporates a prefactor reflecting the time history of the change in the standard volume form ω from time s to time t along the trajectory $\phi_{\tau,t}$ [48]. Equation (81) is Morriss' lemma [22].

For the case of time-independent vector fields $\boldsymbol{\xi}$, the time evolution operator $\phi_{t,s}$ depends only on the time difference $t - s$:

$$\phi_{t,s} = \phi_{t-s,0} \equiv \phi_{t-s}. \tag{82}$$

Moreover, the compressibility κ has no explicit time dependence, $\kappa_\tau = \kappa$. Equation (81) then becomes (setting $s = 0$)

$$\Phi^f_{t,0} \equiv \Phi^f_t = \exp\left[-\int_0^t \mathrm{d}\tau\, \kappa(\phi_{\tau-t}\boldsymbol{x})\right]\phi^*_{-t}. \tag{83}$$

Changing the integration variable to $s \equiv t - \tau$ yields

$$\Phi^f_{t,0} \equiv \Phi^f_t = \exp\left[-\int_0^t \mathrm{d}s\, \kappa(\phi_{-s}\boldsymbol{x})\right]\phi^*_{-t}. \tag{84}$$

That is,

$$f(t, \boldsymbol{x}) = \Phi^f_t f(0, \boldsymbol{x}) = \exp\left[-\int_0^t \mathrm{d}s\, \kappa(\boldsymbol{x}_{-s})\right] f(0, \boldsymbol{x}_{-t}), \tag{85}$$

where $\boldsymbol{x}_{-t} \equiv \phi_{-t}\boldsymbol{x}$ [22,48].

In the derivations to follow we shall *not* use the operator $\Phi^f_{t,s}$, but rather we continue to use standard pull-backs $\phi^*_{t,s}$ and $\phi^*_{s,t}$.

5.2. Calculation of $\phi^*_{t,s} B$

The pull-back $\phi^*_{t,s} B$ satisfies the equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\phi^*_{t,s} B = \phi^*_{t,s}[\mathcal{L}_{\boldsymbol{\xi}_t} B] \equiv \phi^*_{t,s}\big[\mathcal{L}(t)B\big], \tag{86}$$

so that

$$\begin{aligned}\phi^*_{t,s} B &= B + \int_s^t \mathrm{d}\tau\, \frac{\mathrm{d}}{\mathrm{d}\tau}\phi^*_{\tau,s} B \\ &= B + \int_s^t \mathrm{d}\tau\, \phi^*_{\tau,s}\big[\mathcal{L}(\tau)B\big].\end{aligned} \tag{87}$$

We now must evaluate the pull-back $\phi^*_{\tau,s}[\mathcal{L}(\tau)B]$. If we consider the function $\mathcal{L}(\tau)B$ to have *fixed* argument τ, then noting

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\phi^*_{\tau,s}\big[\mathcal{L}(\lambda)B\big]\big|_{\lambda=\tau} = \phi^*_{\tau,s}\big[\mathcal{L}(\tau)\big(\mathcal{L}(\lambda)B\big)\big]\big|_{\lambda=\tau} \tag{88}$$

we have

$$\phi^*_{\tau,s}\big[\mathcal{L}(\tau)B\big] = \mathcal{L}(\tau)B + \int_s^\tau \mathrm{d}\tau'\, \phi^*_{\tau',s}\big[\mathcal{L}(\tau')\big(\mathcal{L}(\tau)B\big)\big], \tag{89}$$

so that, by iterative substitution into (87)

$$\phi^*_{t,s} B = \left[1 + \sum_{n=1,2,\ldots} \int_s^t \mathrm{d}\tau_1 \int_s^{\tau_1} \mathrm{d}\tau_2 \cdots \int_s^{\tau_{n-1}} \mathrm{d}\tau_n\, \mathcal{L}(\tau_n)\mathcal{L}(\tau_2)\mathcal{L}(\tau_1)\right] B. \tag{90}$$

This result expresses the pull-back $\phi^*_{t,s}$ as an operator with *right*-hand-side time-ordering $\tau_n \leqslant \tau_{n-1} \leqslant \cdots \leqslant \tau_1$ (cf. [22,28]). For time-independent $\boldsymbol{\xi}$, the pull-back $\phi^*_{t,s}$ is the exponential operator

$$\phi^*_{t,s} = \mathrm{e}^{(t-s)\mathcal{L}}. \tag{91}$$

5.3. Dyson equations for the pull-back

Consider two time-dependent vector fields $\bar{\boldsymbol{\xi}}(t, \boldsymbol{x})$ and $\boldsymbol{\xi}(t, \boldsymbol{x})$ with associated flows $\overline{\phi}_{t,s}$, $\phi_{t,s}$, and Lie derivatives $\overline{\mathcal{L}}(t) \equiv \overline{\mathcal{L}}_{\bar{\boldsymbol{\xi}}_t}$, $\mathcal{L}(t) \equiv \mathcal{L}_{\boldsymbol{\xi}_t}$. For example, $\boldsymbol{\xi}_t$ could be the unperturbed time evolution, with $\bar{\boldsymbol{\xi}}_t$ the perturbed system dynamics.

There are two relevant Dyson equations, which we write as general relations between pull-backs ϕ^* and $\overline{\phi}^*$:

$$\overline{\phi}^*_{t,s} = \phi^*_{t,s} + \int_s^t \mathrm{d}\tau\, \phi^*_{\tau,s}\big(\overline{\mathcal{L}}(\tau) - \mathcal{L}(\tau)\big)\overline{\phi}^*_{t,\tau}, \tag{92a}$$

$$\overline{\phi}^*_{t,s} = \phi^*_{t,s} + \int_s^t \mathrm{d}\tau\, \overline{\phi}^*_{\tau,s}\big(\overline{\mathcal{L}}(\tau) - \mathcal{L}(\tau)\big)\phi^*_{t,\tau}. \tag{92b}$$

To prove (92a), for example, differentiate both sides of the equation with respect to t:

$$\frac{\mathrm{d}}{\mathrm{d}t}\overline{\phi}^{\,*}_{t,s} = \overline{\phi}^{\,*}_{t,s}\overline{\mathcal{L}}(t), \tag{93a}$$

and

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}t}\left[\phi^*_{t,s} + \int_s^t \mathrm{d}\tau\, \phi^*_{\tau,s}\big(\overline{\mathcal{L}}(\tau) - \mathcal{L}(\tau)\big)\overline{\phi}^{\,*}_{t,\tau}\right] \\ &\quad = \phi^*_{t,s}\mathcal{L}(t) + \phi^*_{t,s}\big(\overline{\mathcal{L}}(t) - \mathcal{L}(t)\big) + \int_s^t \mathrm{d}\tau\, \phi^*_{\tau,s}\big(\overline{\mathcal{L}}(\tau) - \mathcal{L}(\tau)\big)\overline{\phi}^{\,*}_{t,\tau}\overline{\mathcal{L}}(t) \\ &\quad = \left[\phi^*_{t,s} + \int_s^t \mathrm{d}\tau\, \phi^*_{\tau,s}\big(\overline{\mathcal{L}}(\tau) - \mathcal{L}(\tau)\big)\overline{\phi}^{\,*}_{t,\tau}\right]\overline{\mathcal{L}}(t). \end{aligned} \tag{93b}$$

The two sides of equation (92a) are equal for $t = s$, and satisfy the same first-order differential equation in t; they are, therefore, identical. Equation (92b) is proved similarly.

Two additional Dyson equations can be obtained by exchanging $s \leftrightarrow t$.

6. Response theory

Let $f^{(0)}$ be the equilibrium phase space distribution function for time-independent unperturbed dynamics with Lie derivative $\mathcal{L}_{\boldsymbol{\xi}}$. The associated invariant volume form is $\rho^{(0)} = f^{(0)}\omega$, with

$$\mathcal{L}_{\boldsymbol{\xi}}\, \rho^{(0)} = 0. \tag{94}$$

Perturbed dynamics are generated by the vector field $\bar{\boldsymbol{\xi}}(t)$, with associated Lie derivative $\overline{\mathcal{L}}(t)$. Define $\Delta\boldsymbol{\xi}(t) \equiv \bar{\boldsymbol{\xi}}(t) - \boldsymbol{\xi}$ and $\Delta\mathcal{L}(t) \equiv \overline{\mathcal{L}}(t) - \mathcal{L}$, so that

$$\Delta\mathcal{L}(t) = \mathcal{L}_{\Delta\boldsymbol{\xi}(t)}. \tag{95}$$

To illustrate the general theory, we take the unperturbed flow $\boldsymbol{\xi}$ to correspond to the equilibrium Nosé–Hoover system (51), while the flow $\bar{\boldsymbol{\xi}}(t)$ is associated with the perturbed system [46]

$$\dot{q} = \frac{p}{m}, \tag{96a}$$

$$\dot{p} = F(q) - \alpha\zeta p + X(t), \tag{96b}$$

$$\dot{\zeta} = \left[\frac{p^2}{m} - kT\right], \tag{96c}$$

so that $\Delta\boldsymbol{\xi} = (0, X(t), 0)$.

We wish to calculate the average

$$\langle B\rangle(t) = \int_{\mathcal{M}} \big(\overline{\phi}^{\,*}_{t,0}B\big)\rho^{(0)}, \tag{97}$$

where the phase space distribution at $t = 0$ is the equilibrium form $\rho^{(0)}$. Following chapter 8 of [22], we use the Dyson equation (92a) to obtain

$$\begin{aligned}\langle B\rangle(t) &= \int_{\mathcal{M}} (\phi^*_{t,0} B)\rho^{(0)} + \int_0^t \mathrm{d}\tau \int_{\mathcal{M}} \bigl\{\phi^*_{\tau,0}\bigl[\bigl(\overline{\mathcal{L}}(\tau) - \mathcal{L}\bigr)\overline{\phi}^{\,*}_{t,\tau} B\bigr]\bigr\}\rho^{(0)} \\ &= \int_{\mathcal{M}} (\phi^*_{t,0} B)\rho^{(0)} + \int_0^t \mathrm{d}\tau \int_{\mathcal{M}} \bigl\{\phi^*_{\tau,0}\bigl[\Delta\mathcal{L}\overline{\phi}^{\,*}_{t,\tau} B\bigr]\bigr\}\rho^{(0)}. \qquad (98)\end{aligned}$$

The first term is just $\langle B\rangle(0) = \langle B\rangle_0$, the equilibrium average, so that

$$\langle B\rangle(t) - \langle B\rangle_0 = \int_0^t \mathrm{d}\tau \int_{\mathcal{M}} \bigl\{\phi^*_{\tau,0}\bigl[\Delta\mathcal{L}(\tau)\overline{\phi}^{\,*}_{t,\tau} B\bigr]\bigr\}\rho^{(0)} \qquad (99a)$$

$$= \int_0^t \mathrm{d}\tau \int_{\mathcal{M}} \bigl[\Delta\mathcal{L}(\tau)\overline{\phi}^{*}_{t,\tau} B\bigr]\rho^{(0)} \qquad (99b)$$

$$= -\int_0^t \mathrm{d}\tau \int_{\mathcal{M}} \bigl[\overline{\phi}^{\,*}_{t,\tau} B\bigr]\bigl[\Delta\mathcal{L}(\tau)\rho^{(0)}\bigr], \qquad (99c)$$

where we have used $\phi^*_{t,0}\rho^{(0)} = \rho^{(0)}$ and equation (66).

The action of $\Delta\mathcal{L}(\tau)$ on $\rho^{(0)}$ is

$$\Delta\mathcal{L}(\tau)\rho^{(0)} = \bigl(\Delta\mathcal{L}(\tau) f^{(0)}\bigr)\omega + f^{(0)}\bigl(\Delta\mathcal{L}(\tau)\omega\bigr). \qquad (100)$$

If the AIΓ (adiabatic incompressibility of phase space) assumption [22] holds, then

$$\Delta\mathcal{L}(\tau)\omega = \mathrm{div}_\omega\bigl(\Delta\boldsymbol{\xi}(\tau)\bigr)\omega = 0. \qquad (101)$$

That is, the ω-divergence of $\Delta\boldsymbol{\xi}$ vanishes, as is the case, for example, if the time-dependent perturbation derives from a Hamiltonian. We therefore have

$$\Delta\mathcal{L}(\tau)\rho^{(0)} = \bigl(\Delta\mathcal{L}(\tau) f^{(0)}\bigr)\omega. \qquad (102)$$

For the case of the perturbed Nosé–Hoover system discussed above,

$$\Delta\mathcal{L}(\tau) f^{(0)} = +X(t)\frac{\partial}{\partial p} f^{(0)} = -\beta X(t)\left(\frac{p}{m}\right) f^{(0)}, \qquad (103)$$

where we have used the form (54) for $f^{(0)}$, and $\beta = 1/kT$. For more general perturbations, but still assuming AIΓ, we write

$$\Delta\mathcal{L}(\tau)\rho^{(0)} \equiv +\beta X(\tau) J(\boldsymbol{x})\rho^{(0)}, \qquad (104)$$

where $J(\boldsymbol{x})$ is the dissipative flux [22]. We therefore have

$$\langle B\rangle(t) - \langle B\rangle_0 = -\beta \int_0^t \mathrm{d}\tau\, X(\tau) \int_{\mathcal{M}} \bigl[\overline{\phi}^{\,*}_{t,\tau} B\bigr] J(\boldsymbol{x})\rho^{(0)}. \qquad (105)$$

Using the relations

$$\overline{\phi}_{t,\tau} = \overline{\phi}_{t,0}\overline{\phi}_{0,\tau}, \tag{106a}$$

$$\overline{\phi}^{\,*}_{t,\tau} = \overline{\phi}^{\,*}_{0,\tau}\overline{\phi}^{\,*}_{t,0}, \tag{106b}$$

$$1 = \overline{\phi}^{\,*}_{0,\tau}\overline{\phi}^{\,*}_{\tau,0} \tag{106c}$$

and

$$\big[\overline{\phi}^{\,*}_{t,\tau}B\big](\boldsymbol{x}) = \big[\overline{\phi}^{\,*}_{0,\tau}\big[\overline{\phi}^{\,*}_{t,0}B\big]\big](\boldsymbol{x}), \tag{107}$$

we find

$$\langle B\rangle(t) - \langle B\rangle_0 = -\beta\int_0^t \mathrm{d}\tau\, X(\tau)\int_{\mathcal{M}}\big[\overline{\phi}^{\,*}_{t,0}B\big]\overline{\phi}^{\,*}_{\tau,0}\big(J\rho^{(0)}\big). \tag{108}$$

It is now necessary to determine the form $\overline{\phi}^{\,*}_{\tau,0}(J\rho^{(0)})$:

$$\overline{\phi}^{\,*}_{\tau,0}\big(J\rho^{(0)}\big) = \big[\overline{\phi}^{\,*}_{\tau,0}J\big]\big[\overline{\phi}^{\,*}_{\tau,0}\rho^{(0)}\big]. \tag{109}$$

The form $\overline{\phi}^{\,*}_{\tau,0}\rho^{(0)}$ satisfies the differential equation

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}\tau}\overline{\phi}^{\,*}_{\tau,0}\rho^{(0)} &= \overline{\phi}^{\,*}_{\tau,0}\big[\overline{\mathcal{L}}(\tau)\rho^{(0)}\big]\\ &= \overline{\phi}^{\,*}_{\tau,0}\big[\Delta\mathcal{L}(\tau)\rho^{(0)}\big]\\ &= \overline{\phi}^{\,*}_{\tau,0}\big[\big(\beta X(\tau)J\big)\rho^{(0)}\big]\\ &= \beta X(\tau)\big[\overline{\phi}^{\,*}_{\tau,0}J\big]\big[\overline{\phi}^{\,*}_{\tau,0}\rho^{(0)}\big]\end{aligned} \tag{110}$$

with $\overline{\phi}^{\,*}_{\tau,0}\rho^{(0)}|_{\tau=0} = \rho^{(0)}$. The solution to this equation is

$$\overline{\phi}^{\,*}_{\tau,0}\rho^{(0)} = \exp\left[\beta\int_0^\tau \mathrm{d}s\, X(s)J\big(\overline{\phi}_{s,0}\boldsymbol{x}\big)\right]\rho^{(0)}, \tag{111}$$

so the final result is the so-called Kawasaki form for $\langle B\rangle(t)$ [22]

$$\begin{aligned}&\langle B\rangle(t) - \langle B\rangle_0\\ &\quad = -\beta\int_0^t \mathrm{d}\tau\, X(\tau)\int_{\mathcal{M}}\big[\overline{\phi}^{\,*}_{t,0}B\big]\big[\overline{\phi}^{\,*}_{\tau,0}J\big]\exp\left[\beta\int_0^\tau \mathrm{d}s\, X(s)J\big(\overline{\phi}_{s,0}\boldsymbol{x}\big)\right]\rho^{(0)}\\ &\quad \equiv -\beta\int_0^t \mathrm{d}\tau\, X(\tau)\left\langle\big[\overline{\phi}^{\,*}_{t,0}B\big]\big[\overline{\phi}^{\,*}_{\tau,0}J\big]\exp\left[\beta\int_0^\tau \mathrm{d}s\, X(s)J\big(\overline{\phi}_{s,0}\boldsymbol{x}\big)\right]\right\rangle_0.\end{aligned} \tag{112}$$

The usual linear response theory result is easily obtained from (112) by setting

$$\exp\left[\beta\int_0^\tau \mathrm{d}s\, X(s)J\big(\overline{\phi}_{s,0}\boldsymbol{x}\big)\right] \simeq 1, \tag{113}$$

so that

$$\begin{aligned}\langle B\rangle(t) - \langle B\rangle_0 &\simeq -\beta \int_0^t \mathrm{d}\tau\, X(\tau)\big\langle\big[\overline{\phi}^{\,*}_{t,0}B\big]\big[\overline{\phi}^{\,*}_{\tau,0}J\big]\big\rangle_0 \\ &= -\beta \int_0^t \mathrm{d}\tau\, X(\tau)\big\langle B\big(\overline{\phi}_{t,0}\boldsymbol{x}\big)J\big(\overline{\phi}_{\tau,0}\boldsymbol{x}\big)\big\rangle_0 \\ &\equiv -\beta \int_0^t \mathrm{d}\tau\, X(\tau)\big\langle B(t)J(\tau)\big\rangle_0. \end{aligned} \tag{114}$$

7. Summary and conclusion

In this paper we have formulated response theory for non-Hamiltonian systems using concepts and results from the theory of differential forms and time-dependent vector fields on manifolds. Systematic use of the notion of the pull-back enables us to provide a unified and transparent derivation of the response for the general case of time-dependent perturbation of a non-Hamiltonian system.

Our approach is manifestly coordinate-free, so that there can be no question of any coordinate system dependence of the results obtained. In particular, this is true for the generalized Liouville equation satisfied by the phase space distribution function f associated with the form ρ_t, $\rho_t = f_t\omega$.

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