

## FAST TRACK COMMUNICATION

# Impenetrable barriers in phase space for deterministic thermostats

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Online at [stacks.iop.org/JPhysA/42/042001](http://stacks.iop.org/JPhysA/42/042001)**Abstract**

We investigate the relation between the phase-space structures of Hamiltonian and non-Hamiltonian deterministic thermostats. We show that phase-space structures governing reaction dynamics in Hamiltonian systems map to the same type of phase-space structures for the non-Hamiltonian isokinetic equations of motion for the thermostatted Hamiltonian. Our results establish a framework for analyzing thermostat dynamics using concepts and methods developed in reaction rate theory.

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## 1. Introduction

Deterministic thermostats are widely used to simulate equilibrium physical systems described by ensembles other than microcanonical (constant energy and volume,  $(E, V)$ ), such as constant temperature–volume  $(T, V)$  or temperature–pressure  $(T, p)$  [1–5]. Deterministic thermostats are typically obtained by augmenting the phase-space variables of the physical system of interest with a set of additional variables whose role is to alter the standard Hamiltonian system dynamics in such a way that a suitable invariant measure in the system phase space is preserved. In the familiar Nosé–Hoover (NH) thermostat [6, 7], for example, the exact dynamics preserves both an extended energy  $\mathcal{H}$  and a suitable invariant measure, ensuring that, provided the extended system dynamics is effectively ergodic on the timescale of the simulation, the physical system will sample its phase space according to the canonical (constant  $T$ ) measure.

Extended system thermostat dynamics can be either Hamiltonian [6, 8–11] or non-Hamiltonian [7, 12–20]. An important motivation for the formulation of Hamiltonian deterministic thermostats such as the Nosé–Poincaré system [11] is the possibility of using symplectic integration algorithms to compute trajectories [3, 21, 22].

In this approach, an extended Hamiltonian is defined for the physical system plus thermostat variables which incorporates a coordinate-dependent time scaling of Poincaré–Sundman type [23, 24]. Restricting the dynamics to a fixed value (zero) of the extended Hamiltonian results in the system variables sampling their phase space according to, for example, the canonical density [11] (subject to the assumption of ergodicity). The Hamiltonian version of the isokinetic thermostat is described in section 2.

A fundamental question concerning deterministic thermostats has to do with the effective ergodicity of the dynamics on the timescale of the simulation. If the dynamics is not effectively ergodic then trajectory simulations will not generate the correct invariant measure [25, 26]. It has long been recognized, for example, that the dynamical system consisting of a single harmonic oscillator degree of freedom coupled to the NH thermostat variable is not ergodic [27]. A large amount of effort has been expended in attempts to design thermostats exhibiting dynamics more ergodic than the basic NH system [3, 4, 28, 29].

The question of ergodicity in thermostats is conceptually closely related to the problem of statistical versus nonstatistical behavior in the (classical) theory of unimolecular reaction rates [30–32]. Broadly speaking, in this case one would like to know whether a molecule will behave according to a statistical model such as RRKM theory, or whether it will exhibit significant deviations from such a theory, ascribable to nonstatistical dynamics [33, 34]. Such ‘nonstatisticality’, which can arise from a number of dynamical effects, is analogous to the failure of ergodicity in deterministic thermostats.

In recent years, there have been a number of theoretical and computational advances in the application of dynamical systems theory [35–37] to study reaction dynamics and phase-space structure in multimode models of molecular systems and to probe the dynamical origins of nonstatistical behavior [38, 39]. The fundamental chemical concept of the *transition state*, defined as a surface of no return in phase space, has been successfully and rigorously generalized from the well-established 2 degrees of freedom case [40] to systems with  $N \geq 3$  degrees of freedom [39]. Moreover, dynamical indicators exist (determination of reactive phase-space volume, behavior of the reactive flux) to diagnose nonstatistical behavior.

Despite their obvious potential relevance for the questions at issue, there has been relatively little work applying the powerful techniques from modern dynamical systems theory, in particular the theory of multidimensional Hamiltonian systems [36, 37], to study the phase-space structure of deterministic thermostats [2, 8, 27, 29, 41–44]. There appears to be considerable scope for application of these and other approaches [45–47] to the dynamics of deterministic thermostats.

In this communication, we begin the development of a novel theoretical framework for the study of thermostat dynamics. Specifically, we describe how recently developed methods for the analysis of multimode Hamiltonian systems can be applied to investigate the phase-space structure of the isokinetic thermostat [2].

Although not as widely used as the Nosé–Hoover thermostat and its many variants, the non-Hamiltonian version of the isokinetic thermostat has been developed and applied to several problems of chemical interest by Minary *et al* [48, 49]. In this thermostat, the particle momenta are subject to a nonholonomic constraint that keeps the kinetic energy, hence temperature, constant. The resulting dynamics generates a canonical distribution in configuration space [2]. A Hamiltonian version of the isokinetic thermostat was given by Dettmann [2, 8], and this Hamiltonian formulation (see also [50, 51]) is the point of departure for our investigation.

The Hamiltonian formulation of the isokinetic thermostat is presented in section 2. The non-Hamiltonian equations of motion for a Hamiltonian system subject to the isokinetic constraint are shown to correspond to Hamiltonian dynamics at zero energy under an extended

Hamiltonian whose potential is obtained from the physical potential by exponentiation. The extended Hamiltonian dynamics are therefore nonseparable and potentially chaotic (ergodic), even though the physical Hamiltonian might be separable. For the Hamiltonians we consider that the physical potential exhibits a saddle of index 1, as for the case of a bistable reaction profile coupled to one or more transverse confining modes. The bistable mode can play two distinct roles in the theory: it can either be interpreted as a reaction coordinate of physical interest or as a thermalizing thermostat mode [48].

Essential concepts concerning the phase-space structure of multimode Hamiltonian systems, especially the significance of normally hyperbolic invariant manifolds (NHIMs) and their role in the phase-space structure and reaction dynamics of multimode molecular systems with index 1 saddle, are briefly reviewed in section 3.

Our focus in the present study is on saddles of index 1. As mentioned above, the index 1 saddle corresponds to a bistable reaction coordinate coupled to one or more transverse modes, and is a case of fundamental importance for transition state theory. The results obtained in this paper establish the importance of the corresponding structures in the phase space of the isokinetic thermostat. The theory of the phase-space structure in the vicinity of higher index saddles is not as fully developed as the index 1 case, and many open problems remain.

In section 4 we show that the extended Hamiltonian dynamical system satisfies the same conditions satisfied by the physical Hamiltonian that give rise to the phase-space structures discussed in section 3. We then show that these phase-space structures exist for the non-Hamiltonian isokinetic equations of motion for the thermostatted physical Hamiltonian by an explicit mapping. Section 5 concludes.

## 2. The physical Hamiltonian, the extended Hamiltonian and non-Hamiltonian isokinetic thermostat

We begin with a physical Hamiltonian of the standard form

$$H(q, p) = \frac{1}{2}p^2 + \Phi(q), \quad (1)$$

with Hamilton's equations given by

$$\dot{q} = \frac{\partial H}{\partial p} = p, \quad (2a)$$

$$\dot{p} = -\frac{\partial H}{\partial q} = -\Phi_q(q), \quad (2b)$$

where  $(q, p) \in \mathbb{R}^n \times \mathbb{R}^n$  are the physical coordinates and  $\Phi(q)$  is the potential energy. Following Dettmann and Morriss [2, 8], we construct a Hamiltonian system with the property that trajectories on a fixed energy surface of the new Hamiltonian correspond to the trajectories of the physical Hamiltonian (1) which satisfy an isokinetic constraint in the physical coordinates. An extended Hamiltonian  $\mathcal{K}$  is defined as follows:

$$\mathcal{K}(q, \pi) = e^{-\mathfrak{B}\Phi} \mathcal{H}_{\mathfrak{B}}, \quad (3)$$

where  $\mathcal{H}_{\mathfrak{B}}$  is

$$\mathcal{H}_{\mathfrak{B}} = \frac{1}{2} e^{(\mathfrak{B}+1)\Phi} \pi^2 - \frac{1}{2} e^{(\mathfrak{B}-1)\Phi}. \quad (4)$$

Here,  $\mathfrak{B}$  is an arbitrary parameter, and the relation between the momentum variables  $p$  and  $\pi$  is specified below. The value chosen for the parameter  $\mathfrak{B}$  defines a particular time scaling via factorization of  $\mathcal{K}$ ; setting  $\mathfrak{B} = -1$ , for example, ensures that  $\mathcal{H}_{\mathfrak{B}}$  has  $q$ -independent kinetic

energy. (For simplicity we measure energies in units of  $k_B T$ , thus keeping the value of  $T$  implicit.)

The Hamiltonian (3) includes a time scaling factor  $e^{-\mathfrak{B}\Phi}$ , and Hamilton's equations of motion for  $\mathcal{K}$  in physical time  $t$  are

$$\dot{q} = +\frac{\partial \mathcal{K}}{\partial \pi} = e^\Phi \pi \tag{5a}$$

$$\dot{\pi} = -\frac{\partial \mathcal{K}}{\partial q} = -\Phi_q \left[ \frac{1}{2} e^\Phi \pi^2 + \frac{1}{2} e^{-\Phi} \right] \tag{5b}$$

and are manifestly  $\mathfrak{B}$ -independent.

To show that trajectories of the Hamiltonian system (5) with  $\mathcal{K} = 0$  correspond to the trajectories of the physical system (1) satisfying the isokinetic constraint, first note that the time derivative of  $\mathcal{H}_{\mathfrak{B}}$  along trajectories of (5) is given by

$$\dot{\mathcal{H}}_{\mathfrak{B}} = \dot{q} \frac{\partial \mathcal{H}_{\mathfrak{B}}}{\partial q} + \dot{\pi} \frac{\partial \mathcal{H}_{\mathfrak{B}}}{\partial \pi} \tag{6a}$$

$$= \mathfrak{B} \Phi_q e^\Phi \pi \mathcal{H}_{\mathfrak{B}}. \tag{6b}$$

This implies that trajectories of (5) satisfying  $\mathcal{H}_{\mathfrak{B}} = 0$  at  $t = 0$  satisfy  $\mathcal{H}_{\mathfrak{B}} = 0$  for all  $t$  (for arbitrary  $\mathfrak{B}$ ). Using (3), this implies that these trajectories are also confined to the surface  $\mathcal{K} = 0$  for all the time.

The relationship between the Hamiltonian dynamics of (5) on  $\mathcal{K} = 0$  and isokinetic trajectories of (1) is made apparent by making the *noncanonical* transformation of variables

$$q \mapsto q, \tag{7a}$$

$$\pi \mapsto e^{-\Phi(q)} p. \tag{7b}$$

This coordinate transformation is clearly invertible and is, in fact, a diffeomorphism (as differentiable as  $\Phi$ ). Applying (7) to  $\mathcal{H}_{\mathfrak{B}}$  gives

$$\mathcal{H}_{\mathfrak{B}} = \frac{1}{2} e^{(\mathfrak{B}-1)\Phi} (p^2 - 1) \tag{8}$$

from which we can immediately conclude that trajectories of the Hamiltonian system (5) with  $\mathcal{K} = \mathcal{H}_{\mathfrak{B}} = 0$  automatically satisfy the isokinetic condition

$$p^2 = 1, \tag{9}$$

in the physical coordinates  $(q, p)$ . Substituting relation (7) into (5) we obtain equations of motion for  $(q, p)$ :

$$\dot{q} = p \tag{10a}$$

$$\dot{p} = -\Phi_q \frac{1}{2} (p^2 + 1) + p(\Phi_q \cdot \dot{q}) = -\Phi_q - \alpha p, \tag{10b}$$

where  $\alpha \equiv -\Phi_q \cdot p$  and we have used the constraint  $p^2 = 1$ . Equations (10) are the isokinetic equations of motion for the thermostatted physical Hamiltonian (1) in physical time  $t$ , obtained via Gauss' principle of least constraint [2].

By design, the isokinetic dynamics (10) generates a canonical distribution in the coordinates  $q$  [2, 8]. Minary *et al* [48] have shown that the addition of thermalizing degrees of freedom to the physical Hamiltonian (1) can facilitate the attainment of the correct canonical distribution in  $q$ -space. If  $H$  describes a collection of uncoupled oscillators, the addition

of a bistable thermalizing degree of freedom renders the Hamiltonian dynamics under  $\mathcal{K}$  isomorphic to that of a reactive degree of freedom coupled to several bath modes, so that we can obtain useful insights into the thermostat dynamics using methods recently developed for multidimensional Hamiltonian systems. Alternatively, if  $H$  describes a reactive mode coupled to bath modes, then the  $\mathcal{K}$  dynamics is already in an appropriate form for the phase-space analysis described in the following section.

### 3. Phase-space structures on a fixed energy surface

Our analysis of thermostat dynamics will be carried out in phase space, using the tools and framework for reaction type dynamics of Hamiltonian systems developed in [38, 39, 52–58]. We will show in section 4 that these results apply both to the physical Hamiltonian system (2) and to the extended Hamiltonian system (5). Here we give a brief summary of the setting and relevant results from these references.

The starting point for identifying a region of phase space relevant to reaction is to locate an equilibrium point of Hamilton's equations, denoted  $(q^*, p^*)$ , that is of saddle-center-center stability type. By this we mean that the matrix associated with the linearization of Hamilton's equations about this equilibrium point has two real eigenvalues of equal magnitude, with one positive and one negative, and  $n - 1$  purely imaginary complex conjugate pairs of eigenvalues. We will assume that the purely imaginary eigenvalues satisfy a generic nonresonance condition in the sense that they are independent over the rational numbers (this is discussed in more detail in section 4).

We will assume that such an equilibrium point is present in the physical system (2) and we will show that the same type of equilibrium point exists for the extended Hamiltonian system (5) in section 4. However, the discussion in this section applies to any type of Hamiltonian system near the same type of equilibrium point. Without loss of generality we can assume that  $(q^*, p^*)$  is located at the origin, and we denote its energy by  $H(q^*, p^*) \equiv h^*$ .

We will be concerned with geometrical structures in a neighborhood of phase space containing the saddle-center-center type equilibrium point. We emphasize this fact by denoting the neighborhood by  $\mathcal{L}$ ; this region is to be chosen so that a new set of coordinates can be constructed (the normal form coordinates) in which the Hamiltonian can be expressed (the normal form Hamiltonian) such that it provides an integrable nonlinear approximation to the dynamics which yields phase-space structures to within a given desired accuracy.

For  $h - h^*$  sufficiently small and positive, locally the  $((2n - 1)$ -dimensional) energy surface  $\Sigma_h$  has the structure of  $S^{2n-2} \times \mathbb{R}$  in the  $2n$ -dimensional phase space. The energy surface  $\Sigma_h$  is split locally into two components, 'reactants' (R) and 'products' (P), by a  $((2n - 2)$ -dimensional) 'dividing surface' (DS( $h$ )) that is diffeomorphic to  $S^{2n-2}$ . The dividing surface that we construct has the following properties:

- The only way that trajectories can evolve from reactants (R) to products (P) (and vice versa), without leaving the local region  $\mathcal{L}$ , is through DS( $h$ ). In other words, initial conditions on this dividing surface specify all reacting trajectories.
- The dividing surface is free of local re-crossings; any trajectory which crosses it must leave the neighborhood  $\mathcal{L}$  before it might possibly cross again.
- The dividing surface minimizes the (directional) flux.

The fundamental phase-space building block that allows the construction of a dividing surface with these properties is a particular *normally hyperbolic invariant manifold* (NHIM) which, for fixed energy  $h > h^*$ , will be denoted by NHIM( $h$ ). The NHIM( $h$ ) is diffeomorphic to  $S^{2n-3}$  and forms the natural *dynamical equator* of the dividing surface: the dividing surface

is split by this equator into  $(2n - 2)$ -dimensional hemispheres, each diffeomorphic to the open  $(2n - 2)$  ball,  $B^{2n-2}$ . We will denote these hemispheres by  $DS_f(h)$  and  $DS_b(h)$  and call them the ‘forward reactive’ and ‘backward reactive’ hemispheres, respectively.  $DS_f(h)$  is crossed by trajectories representing ‘forward’ reactions (from reactants to products), while  $DS_b(h)$  is crossed by trajectories representing ‘backward’ reactions (from products to reactants).

The  $(2n - 3)$ -dimensional NHIM( $h$ ) is an (unstable) invariant subsystem which, in chemistry terminology, corresponds to the energy surface of the ‘activated complex’ [40, 59].

The NHIM( $h$ ) is of saddle stability type, having  $(2n - 2)$ -dimensional stable and unstable manifolds  $W^s(h)$  and  $W^u(h)$  that are diffeomorphic to  $S^{2n-3} \times \mathbb{R}$ . Being of co-dimension one<sup>3</sup> with respect to the energy surface, these invariant manifolds act as separatrices, partitioning the energy surface into ‘reacting’ and ‘nonreacting’ parts.

These phase-space structures can be computed via an algorithmic procedure based on Poincaré–Birkhoff normalization [38, 39, 52]. This involves developing a new set of coordinates, the *normal form coordinates*,  $(\bar{q}, \bar{p})$ , which are realized through a symplectic coordinate transformation from the original, physical coordinates,

$$T(q, p) = (\bar{q}, \bar{p}), \quad (11)$$

which, in a local neighborhood  $\mathcal{L}$  of the equilibrium point, ‘unfolds’ the dynamics into a ‘reaction coordinate’ and ‘bath modes’. Expressing  $H$  in the new coordinates,  $(\bar{q}, \bar{p})$ , via

$$H_{\text{NF}}(\bar{q}, \bar{p}) = H(T^{-1}(q, p)) \quad (12)$$

gives  $H_{\text{NF}}$  in a simplified form. The normalization procedure can also be adapted to yield explicit expressions for the coordinate transformations,  $T(q, p) = (\bar{q}, \bar{p})$  and  $T^{-1}(\bar{q}, \bar{p}) = (q, p)$ , between the normal form (NF) coordinates and the original coordinates<sup>4</sup>. These coordinate transformations are essential for physical interpretation of the phase-space structures that we construct in normal form coordinates since they allow us to transform these structures back into the original ‘physical’ coordinates.

The nonresonance condition implies that the normal form procedure yields an explicit expression for the normalized Hamiltonian  $H_{\text{NF}}$  as a function of  $n$  local integrals of motion:

$$H_{\text{NF}} = H_{\text{NF}}(I_1, I_2, \dots, I_n). \quad (13)$$

The integral,  $I_1$ , corresponds to a ‘reaction coordinate’ (saddle-type DoF):

$$I_1 = \bar{q}_1 \bar{p}_1. \quad (14)$$

The integrals  $I_k$ , for  $k = 2, \dots, n$ , correspond to ‘bath modes’ (center-type DoFs):

$$I_k = \frac{1}{2} (\bar{q}_k^2 + \bar{p}_k^2). \quad (15)$$

The integrals provide a natural definition of the term ‘mode’ that is appropriate in the context of reaction, and their existence is a consequence of the (local) integrability in a neighborhood of the equilibrium point of saddle-center-...-center stability type. Moreover, the expression of the normal form Hamiltonian in terms of the integrals provides us with a way to partition the energy between the different modes<sup>5</sup>.

<sup>3</sup> Briefly, the co-dimension of a submanifold is the dimension of the space in which the submanifold exists, minus the dimension of the submanifold. The significance of a submanifold being ‘co-dimension one’ is that it is one less dimension than the space in which it exists. Therefore it can ‘divide’ the space and act as a separatrix, or barrier, to transport.

<sup>4</sup> The original coordinates  $(q, p)$  had an interpretation as configuration space coordinates and momentum coordinates. The normal form coordinates  $(\bar{q}, \bar{p})$ , in general, do not have such a physical interpretation since both  $\bar{q}$  and  $\bar{p}$  are nonlinear functions of both  $q$  and  $p$ .

<sup>5</sup> The normal form algorithm that yields all of these results can be applied to realistic molecular Hamiltonians with software available at <http://lacms.maths.bris.ac.uk/publications/software/index.html>.

The  $n$  integrals, the normalized Hamiltonian expressed as a function of the integrals and the transformation between the normal form coordinates and the physical coordinates are the key to practically realizing the phase-space structures described at the beginning of this section. The approximate integrability of Hamilton's equations in the reaction region allows a precise and quantitative understanding of all possible trajectories in this region. It also provides a natural construction of an energy dependent reaction coordinate whose properties are determined solely by the Hamiltonian dynamics, as opposed to the need for *a priori* definitions of possible candidates for reaction coordinates [60].

The  $n$  integrals of the motion defined in the neighborhood of the reaction region give rise to further phase-space structures, and therefore constraints on the motion, in addition to those described at the beginning of this section. The common level sets of all the integrals are examples of invariant *Lagrangian submanifolds* [61–63], which have the geometrical structure of two disjoint  $n$ -dimensional toroidal cylinders, denoted  $\mathbb{R} \times \mathbb{T}^{n-1}$ , i.e. the Cartesian product of a line with  $n - 1$  copies of the circle.

In the following section we show how all of this phase-space structure exists for thermostatted dynamics of the physical Hamiltonian (1) in physical time  $t$ .

#### 4. Microcanonical phase-space structure: Hamiltonian and corresponding non-Hamiltonian thermostatted systems

In this section we will show that if the phase-space structure described in section 3 exists for the physical Hamiltonian system (2), it also exists in the phase space of the non-Hamiltonian isokinetic equations of motion (10) corresponding to the thermostatted dynamics of the physical Hamiltonian (1) in physical time  $t$ . This is accomplished in three steps by showing:

- (1) If the physical Hamiltonian system (2) has an equilibrium point at the origin of saddle-center-...-center stability type, then the Hamiltonian system defined by (5) corresponding to the Hamiltonian isokinetic thermostat has an equilibrium point also at the origin of saddle-center-...-center stability type. Moreover (and significantly), we show that the equilibrium points in these two systems satisfy the same nonresonance condition.
- (2) The energy of the saddle-center-...-center type equilibrium point of (5) is negative, but it can be brought sufficiently close to zero so that the microcanonical geometrical structures described in section 3 exist on the zero-energy surface of (5).
- (3) The geometrical structures on the zero-energy surface of (5) map to geometrical structures in the phase space of the non-Hamiltonian thermostatted system corresponding to (10).

We begin with step 1. We assume that (2) has an equilibrium point at  $(q, p) = (q^*, p^*) = (0, 0)$ . From (1), the energy of this equilibrium point is  $H(0, 0) = \Phi(0)$ .

The stability of the equilibrium point is determined by the eigenvalues of the derivative of the Hamiltonian vector field evaluated at the equilibrium point. This is given by the  $2n \times 2n$  matrix:

$$M_{\text{sys}} = \begin{pmatrix} 0_{n \times n} & \text{id}_{n \times n} \\ -\Phi_{qq}(0) & 0_{n \times n} \end{pmatrix}, \quad (16)$$

where  $0_{n \times n}$  denotes the  $n \times n$  matrix of zeros and  $\text{id}_{n \times n}$  denotes the  $n \times n$  identity matrix. We require the equilibrium point to be of saddle-center-...-center stability type. This means that the  $2n \times 2n$  matrix  $M_{\text{sys}}$  has eigenvalues  $\pm\lambda, \pm i\omega_i, i = 2, \dots, n$  where  $\lambda$  and  $\omega_i$  are real.

Eigenvalues  $\gamma$  of  $M_{\text{sys}}$  are obtained by solving the characteristic equation  $\det(M_{\text{sys}} - \gamma \text{id}_{2n \times 2n}) = 0$ . From theorem 3 of [64], the block structure of the  $2n \times 2n$  matrix  $M_{\text{sys}}$  implies that

$$\det(M_{\text{sys}} - \gamma \text{id}_{2n \times 2n}) = \det(\Phi_{qq}(0) + \gamma^2 \text{id}_{n \times n}) = 0 \quad (17)$$

so that the  $2n$  eigenvalues  $\gamma$  are given in terms of  $\sigma$ , the eigenvalues of the  $n \times n$  Hessian matrix  $\Phi_{qq}(0)$  associated with the potential as follows:

$$\gamma_k, \gamma_{k+n} = \pm\sqrt{-\sigma_k}, \quad k = 1, \dots, n. \tag{18}$$

Therefore, if  $\Phi(q)$  has a rank-one saddle at  $q = 0$ , so that one eigenvalue is strictly negative and the rest are strictly positive, then  $(q, p) = (0, 0)$  is a saddle-center-center type equilibrium point for (2) as described above.

We discuss the nonresonance condition in more detail. Suppose  $\sigma_1 < 0$  and  $\sigma_i > 0$ ,  $i = 2, \dots, n$ . Then the nonresonance condition satisfied by the purely imaginary eigenvalues is given by  $(m_2, \dots, m_n) \cdot (\gamma_2, \dots, \gamma_n) \neq 0$  for all integer vectors  $(m_2, \dots, m_n)$  whose entries are not all zero (where ‘ $\cdot$ ’ denotes the scalar product). The nonresonance condition is responsible for the existence of the  $n - 1$  (local) integrals of motion  $I_2, \dots, I_n$ .

Next, we consider the Hamiltonian system (5) corresponding to the Hamiltonian isokinetic thermostat. It is easy to verify that  $(q, \pi) = (0, 0)$  is an equilibrium point for (5) with energy  $\mathcal{K}(0, 0) = -\frac{1}{2}e^{-\Phi(0)}$ .

Proceeding as above, we determine the stability of this equilibrium point by computing the matrix associated with the linearization of (5) at the equilibrium point:

$$M_{\text{therm}} = \begin{pmatrix} 0_{n \times n} & \text{id}_{n \times n} e^{+\Phi(0)} \\ -\Phi_{qq}(0) (\frac{1}{2} e^{-\Phi(0)}) & 0_{n \times n} \end{pmatrix}. \tag{19}$$

The  $2n$  eigenvalues of  $M_{\text{therm}}$ , which we denote as  $\bar{\gamma}$ , can be computed by exactly the same type of calculations as above. The resulting eigenvalues are given in terms of the eigenvalues of the potential Hessian as follows:

$$\bar{\gamma}_k, \bar{\gamma}_{k+n} = \pm\sqrt{-\frac{\sigma_k}{2}}, \quad k = 1, \dots, n. \tag{20}$$

Therefore, it is clear that if the potential of the physical Hamiltonian,  $\Phi(q)$ , has a rank-one saddle at  $q = 0$ , so that one eigenvalue is strictly negative and the rest are strictly positive, then  $(q, \pi) = (0, 0)$  is a saddle-center-center type equilibrium point for (5).

Moreover, since  $\bar{\gamma} = \frac{1}{\sqrt{2}}\gamma$  it follows by comparing (18) with (20) that if the imaginary parts of the eigenvalues associated with the saddle for the physical Hamiltonian satisfy a nonresonance condition, then they satisfy a nonresonance condition for the saddle associated with the Hamiltonian isokinetic thermostat, i.e  $(m_2, \dots, m_n) \cdot (\gamma_2, \dots, \gamma_n) \neq 0$  implies that  $(m_2, \dots, m_n) \cdot \frac{1}{\sqrt{2}}(\gamma_2, \dots, \gamma_n) = (m_2, \dots, m_n) \cdot (\bar{\gamma}_2, \dots, \bar{\gamma}_n) \neq 0$ .

Now consider step 2. As we showed above, the saddle-center-center type equilibrium point  $(q, \pi) = (0, 0)$  of 5 has energy  $\mathcal{K}(0, 0) = -\frac{1}{2}e^{-\Phi(0)} < 0$ . However, we are only interested in the dynamics on the  $\mathcal{K} = 0$  energy surface. The point here is that all of the phase-space structures described in section 3 exist for energies ‘above and sufficiently close’ to the energy of the saddle-center-center type equilibrium point, and the question is whether or not  $-\frac{1}{2}e^{-\Phi(0)} < 0$  is close enough to zero so that the phase-space structures described in section 3 exist on the  $\mathcal{K} = 0$  energy surface. This can easily be arranged by making  $\Phi(0)$  larger by adding an appropriate constant to  $\Phi(q)$  or by changing the value of the temperature  $T$ .

The final step 3 is to show that the phase-space structure of (5) on  $\mathcal{K} = 0$  exists for the isokinetic equations of motion (10) corresponding to the thermostatted dynamics of the physical Hamiltonian (1) in physical time  $t$ .

Step 3 follows from general results that show that invariant manifolds and their stability properties are preserved under differentiable, invertible (with differentiable inverse) coordinate transformations (i.e. they are preserved under differentiable conjugacies). We emphasize that

these results are ‘well known’ and appear in a variety of places throughout the literature, e.g., [65, 66].

These general results allow us to make the following conclusions:

- Under the map (7) the  $(2n - 1)$ -dimensional invariant energy surface of the effective Hamiltonian system (5) maps to a  $(2n - 1)$ -dimensional invariant manifold for the non-Hamiltonian isokinetic equations of motion for the thermostatted physical Hamiltonian (1) in physical time  $t$  defined by (10).
- Under the map (7) the  $(2n - 3)$ -dimensional NHIM, its  $(2n - 2)$ -dimensional stable and unstable manifolds, the  $n$ -dimensional invariant Lagrangian submanifolds and the  $(2n - 2)$ -dimensional dividing surface map to a  $(2n - 3)$ -dimensional NHIM, its  $(2n - 2)$ -dimensional stable and unstable manifolds,  $n$ -dimensional invariant submanifolds and a  $(2n - 2)$ -dimensional dividing surface in the  $(2n - 1)$ -dimensional invariant manifold in the  $2n$ -dimensional phase space of the non-Hamiltonian isokinetic equations of motion for the thermostatted physical Hamiltonian (1) in physical time  $t$  defined by (10).

## 5. Summary and outlook

In this paper we have examined the relation between phase-space structures in Hamiltonian and non-Hamiltonian thermostats. In particular, we have established the existence of a mapping between invariant phase-space structures in the phase space of the extended Hamiltonian for the isokinetic thermostat and corresponding structures in the phase space of the non-Hamiltonian Gaussian isokinetic thermostat.

Our results establish a conceptual link between the question of thermostat ergodicity and the issue of statisticality in unimolecular isomerization reactions. The existence of normally hyperbolic invariant manifolds in both the physical and extended Hamiltonian phase spaces means that recently developed methods for the analysis of isomerization dynamics can be applied to the thermostat problem. Numerical studies of the isokinetic thermostat based on the ideas presented here are currently in progress.

Finally, we note that the approach presented here for the Hamiltonian isokinetic thermostat is in principle applicable to other thermostats. Although the popular Nosé–Hoover thermostat [6, 7] and its many variants such as the Nosé–Hoover chain thermostat [28] are essentially non-Hamiltonian dynamical systems, the analysis outlined in the present paper could be applied to Hamiltonian thermostats such as the Nosé–Poincaré system [11].

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