Hamiltonian reformulation and pairing of Lyapunov exponents for Nosé-Hoover dynamics

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The Nosé Hamiltonian is adapted, leading to a derivation of the Nosé-Hoover equations of motion which does not involve time transformations, and in which the degree of freedom corresponding to the external reservoir is treated on the same footing as those of the rest of the system. In this form it is possible to prove the conjugate pairing rule for Lyapunov exponents of this system. [S1063-651X(97)07202-4]

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I. INTRODUCTION

The Nosé Hamiltonian [1,2]

$$H_N(\mathbf{q},s;\boldsymbol{\pi},p_s;\lambda)=\sum_{i=1}^{N}\frac{|\boldsymbol{\pi}_i|^2}{2m_i s^2}+\varphi(\mathbf{q})+\frac{p_s^2}{2Q}+gkT\ln s \tag{1}$$

is used to model a system of N particles interacting with a thermal reservoir at temperature T, represented by the coordinate s with its conjugate momentum p_s. g is a constant which depends on the number of degrees of freedom of the system. If we interpret the time variable λ as a nonphysical parameter, with physical time intervals defined by $dt=d\lambda/s$ and physical momentum $\mathbf{p}_i=d\mathbf{q}_i/dt=\boldsymbol{\pi}_i/s$, a uniform (microcanonical) probability measure on the full $(\mathbf{q},\boldsymbol{\pi},s,p_s)$ phase space reduces to a canonical probability measure on the system variables $(\mathbf{q},\mathbf{p})$, as long as $g=3N+1$. Thus a molecular dynamics simulation may be used to model canonical, as well as microcanonical ensembles, as long as the extended system dynamics is ergodic. Refer to Ref. [3] for a more complete discussion and review. Numerical results suggest that the ergodic assumption may be reasonable for all but the very smallest systems [4]. It is possible to make a number of modifications of the time and momentum variables in H_N to obtain other dynamical systems which generate the canonical ensemble [5,6].

Hoover [7] pointed out that the equations in terms of the physical variables $(\mathbf{q},\mathbf{p},t)$ and $\zeta=p_s/Q$ take on a particularly simple form:

$$\dot{\mathbf{q}}_i=\mathbf{p}_i/m_i, \tag{2}$$

$$\dot{\mathbf{p}}_i=-\nabla_i\varphi-\zeta\mathbf{p}_i, \tag{3}$$

$$\dot{\zeta}=\frac{1}{Q}\left(\sum_{i=1}^{N}\frac{|\mathbf{p}|_i^2}{m_i}-gkT\right), \tag{4}$$

$$\dot{s}=\zeta s. \tag{5}$$

Note that the first three equations form a closed set; s is now redundant. In this form, it is apparent that ζ acts as a kind of thermostat acting on the kinetic energy of the N-particle system. $\dot{\zeta}$ is proportional to the difference between the kinetic energy and $gkT/2$, so that when the kinetic energy rises above this value, ζ increases, raising the damping term in the equation for $\dot{\mathbf{p}}$, and thus reducing the kinetic energy. In the Hoover representation the equilibrium distribution is changed because of the time scaling, however, the canonical distribution in the system variables is recovered by setting $g=3N$.

The real utility of this approach, however, is to nonequilibrium systems. In a nonequilibrium simulation in which energy is being pumped through the system such a thermostat permits the system to approach a steady state while remaining homogeneous; there are alternative approaches involving boundaries which do not share this property [8–10]. Another important thermostatting method based on Gauss's principle of least constraint [11] uses ζ as an explicit function of the coordinates rather than a variable in its own right [12]. The Nosé-Hoover and Gaussian thermostats give the same averages and time correlation functions in the thermodynamic limit [13]. The important point to note here is that any representation of a nonequilibrium steady state must contain some reference to an external heat reservoir. A possible advantage of the Nosé-Hoover scheme over the Gaussian approach is that this reservoir is explicitly included as a separate degree of freedom, so that it may be treated on a similar footing as the rest of the system. Recently a number of modifications and extensions to the Nosé-Hoover method have been proposed [14–17].

Lyapunov exponents (defined in Sec. III) are important in the study of nonequilibrium systems, giving information on the chaotic instability, and providing an important link between the microscopic and macroscopic properties, since the sum of the exponents gives the average rate of phase space expansion, which can then be related to entropy production, and hence transport coefficients. The conjugate pairing rule for Lyapunov exponents is the property that there is a constant C such that for every exponent λ, $C-\lambda$ is also an exponent, with the possible exception of one or two exponents which are fixed to be zero by symmetry considerations. It was first discussed in Refs. [12,18]. The conjugate pairing rule permits the sum of the exponents to be calculated from the largest and smallest, which are the easiest to evaluate numerically. Hamiltonian systems obey conjugate pairing with $C=0$, that is, the exponents come in $\pm$ pairs [19]. Systems with a constant damping factor pair with C proportional to this factor [20]. Recently the conjugate pairing rule has been shown to hold for systems containing a Gaussian

thermostat [21], where C is minus the average value of the thermostatting multiplier α (analogous to ζ here). In this case there are two zero exponents which do not pair, which arise from the time translation symmetry, and the conserved kinetic energy.

Note that the Lyapunov exponents depend on the variables used to define the phase space if the equations relating different coordinate systems involve exponential functions of time. This means that, although it is trivial to prove that the Lyapunov exponents obtained using the original Nosé variables pair to zero, because the equations of motion are derived from a Hamiltonian, it is much harder to make statements about the Hoover variables, particularly since a different time variable is used. Here the total phase space contraction, which is given by minus the sum of the Lyapunov exponents, is proportional to the average of ζ, which is nonzero for a nonequilibrium steady state. Since the sum of the exponents is less than zero, it is clear that the exponents are quite different to the Nosé values, for which the sum is trivially zero.

Section II of this paper shows how to write the Nosé Hamiltonian in a form which treats the system and reservoir variables on equal footing, leading to a proof of the conjugate pairing rule in Sec. III , along the lines of the proof in Ref. [21].

II. UNIFIED HAMILTONIAN FORMALISM

In the form given by Nosé [Eq. (1)], the reservoir variable s is treated quite differently than the other coordinates in that the system kinetic term is divided by s^2 whereas the reservoir kinetic term is not. In addition, the time λ corresponding to the Hamiltonian does not correspond to physical time. Here H_N is transformed to alleviate both of these deficiencies.

The unified form of the Hamiltonian is obtained by transforming to a new coordinate $\sigma = \ln s$. This type of transformation is described in Sec. 9.2 of Ref. [22], and uses a generating function of the form

$$F_2(\mathbf{q},s;\boldsymbol{\pi},p_\sigma;\lambda) = \sum_{i=1}^{N} \mathbf{q}_i \cdot \boldsymbol{\pi}_i + p_\sigma \ln s, \tag{6}$$

leading to a new momentum $p_\sigma = s p_s$, and transformed Hamiltonian

$$H_T(\mathbf{q},\sigma;\boldsymbol{\pi},p_\sigma;\lambda) = \frac{e^{-2\sigma}}{2}\left(\sum_{i=1}^{N} \frac{|\boldsymbol{\pi}_i|^2}{m_i} + \frac{p_\sigma^2}{Q} \right) + \varphi(\mathbf{q}) + gkT\sigma. \tag{7}$$

Note that the form of the potential is also simpler in this representation. The masses may also be scaled out: Construct $3N+1$ dimensional vectors $\mathbf{X} = (\mathbf{q}_i\sqrt{m_i}, \sigma\sqrt{Q})$ and $\mathbf{P} = (\boldsymbol{\pi}_i/\sqrt{m_i}, p_\sigma/\sqrt{Q})$, and write $\Phi(\mathbf{X}) = -\sigma$ and $\phi(\mathbf{X}) = \varphi(\mathbf{q}) + gkT\sigma$. The Hamiltonian may then be written in a unified form as

$$H_U(\mathbf{X};\mathbf{P};\lambda) = \frac{|\mathbf{P}|^2}{2} e^{2\Phi(\mathbf{X})} + \phi(\mathbf{X}). \tag{8}$$

The final transformation which eliminates the need for an unphysical time variable follows similarly to the Hamiltonian for the Gaussian thermostat [23]. First add a constant to ϕ so that the initial (and hence at all times) value of H_U is zero. It is easily verified that multiplying a zero Hamiltonian by an arbitrary function scales the time, but has no other effect on the equations of motion. Thus the final form of the Hamiltonian is

$$H_F(\mathbf{X};\mathbf{P};t) = \frac{|\mathbf{P}|^2}{2} e^{\Phi(\mathbf{X})} + \phi(\mathbf{X}) e^{-\Phi(\mathbf{X})}. \tag{9}$$

This transformation is equivalent to multiplying H_N in Eq. (1) by s, which is a particularly simple method of generating Eqs. (2)–(5) without the use of unphysical time variables.

It is also convenient to introduce a few more $3N+1$ dimensional vectors,

$$\mathbf{V} = \mathbf{P} e^{\Phi}, \tag{10}$$

$$\mathbf{F} = -\nabla\Phi, \tag{11}$$

$$\mathbf{f} = -\nabla\phi, \tag{12}$$

in terms of which the condition $H_F = 0$ becomes

$$\frac{|\mathbf{V}|^2}{2} + \phi = 0, \tag{13}$$

and Hamilton's equations of motion reduce to

$$\dot{\mathbf{X}} = \mathbf{V}, \tag{14}$$

$$\dot{\mathbf{V}} = |\mathbf{V}|^2\mathbf{F} - \mathbf{F}\cdot\mathbf{V}\mathbf{V} + \mathbf{f}. \tag{15}$$

As an example, let us consider the Nosé-Hoover oscillator of Ref. [4]. For a single particle in a one dimensional harmonic oscillator potential, $\varphi = m\omega^2 q^2/2$. Then the Hamiltonian becomes

$$H_F(q,\sigma;\pi,p_\sigma;t) = [\pi^2/(2m) + p_\sigma^2/(2Q)]e^{-\sigma} + (m\omega^2 q^2/2 + gkT\sigma)e^{\sigma}, \tag{16}$$

and the vectors we introduced above are

$$\mathbf{X} = (q\sqrt{m}, \sqrt{Q}\ln s), \tag{17}$$

$$\mathbf{V} = (\pi/(s\sqrt{m}), p_\sigma/(s\sqrt{Q})) = (p/\sqrt{m}, \sqrt{Q}\zeta), \tag{18}$$

$$\mathbf{F} = (0, 1/\sqrt{Q}), \tag{19}$$

$$\mathbf{f} = (-\omega^2 q\sqrt{m}, -gkT/\sqrt{Q}). \tag{20}$$

In this form it is straightforward to show that Eqs. (14) and (15) are equivalent to Hoover's form of the equations, Eqs. (2)–(5). The decoupling of the s (or σ) equation occurs because $\mathbf{F}$ and $\mathbf{f}$ are independent of s.

III. CONJUGATE PAIRING

The equations of motion given previously are now in a form suitable for a proof of the conjugate pairing rule for

Lyapunov exponents. Note that the coordinates used are the same (apart from constants related to the masses) as the Nosé-Hoover thermostat, except that s is replaced by σ. The components of V are proportional to the physical momentum $\mathbf{p}$ and ζ. Since the equations do not depend on σ, the Lyapunov exponents obtained contain one extra zero exponent, but otherwise are the same as the other $6N+1$ equations considered separately.

The argument given here closely follows Ref. [21], so the presentation will be correspondingly brief. It is convenient to group $\mathbf{X}$ and $\mathbf{V}$ together to form a point Γ in $6N+2$ dimensional phase space. Time dependent matrices T and L are defined, giving the infinitesimal and finite evolution of linear perturbations $\delta\Gamma$ as follows:

$$\delta\dot{\Gamma}(t)=T(t)\,\delta\Gamma(t), \tag{21}$$

$$\delta\Gamma(t)=L(t)\,\delta\Gamma(0). \tag{22}$$

The Lyapunov exponents are defined as the logarithms of the eigenvalues of Λ, where

$$\Lambda=\lim_{t\to\infty}[L^{T}(t)L(t)]^{1/(2t)}. \tag{23}$$

Two of the Lyapunov exponents are zero due to the fact that perturbations along the flow simply add a constant to the time, and the conservation of the value of the Hamiltonian, Eq. (13), which is the total (scaled) energy of the system and reservoir. Of course the energy of the system alone is not conserved, as it maps out a canonical distribution.

The conjugate pairing clearly does not include these two exponents, so perturbations along the flow and those which alter the value of the Hamiltonian must be eliminated before the pairing is apparent. This is achieved by considering $6N$ perturbations, none of which are along the flow or alter the total energy. They are measured with respect to a basis in a $6N$ dimensional subspace which rotates with the trajectory in order to enforce these properties. In particular, $\delta\mathbf{X}$ is always perpendicular to $\mathbf{V}$ (in $3N+1$ dimensional coordinates), and $\delta\mathbf{V}$ has a component parallel to $\mathbf{V}$ which is fixed by energy conservation. As the perturbed trajectory evolves, it will always have the same conserved energy, but $\delta\mathbf{X}$ may not remain perpendicular to $\mathbf{V}$. The perturbed trajectory will, however, cross the $6N$ dimensional space at some time t' different to t, so the above conditions may be enforced by allowing the perturbed trajectory to evolve at a rate different to the original. The Lyapunov exponents obtained using this approach are the same as for the full $6N+2$ dimensional space, with the exception of the two zeros. These issues are discussed in more detail in Ref. [21], the only difference being that here the phase space is not compact. The arguments follow through exactly the same, however, if ergodicity is assumed, as it is when deriving the canonical distribution (Sec. I).

The first step is to choose an orthonormal basis in $3N+1$ dimensional space, $\{\mathbf{e}_0,\mathbf{e}_i\}$, with i ranging from 1 to $3N$, as it will henceforth. $\mathbf{e}_0$ is parallel to $\mathbf{V}$,

$$\mathbf{V}=V\mathbf{e}_0, \tag{24}$$

with $V=|\mathbf{V}|$ and all the $\mathbf{e}_i$ are perpendicular to $\mathbf{V}$. This basis is used for both $\mathbf{X}$ and $\mathbf{V}$ subspaces. The equations of motion (14) and (15) determine the time evolution of V and $\mathbf{e}_0$,

$$\dot{V}=\mathbf{f}\cdot\mathbf{e}_0, \tag{25}$$

$$\dot{\mathbf{e}}_0=\sum_i\,(V\mathbf{F}+V^{-1}\mathbf{f})\cdot\mathbf{e}_i\mathbf{e}_i. \tag{26}$$

The equations of motion for the other basis vectors are somewhat arbitrary, but the natural choice which preserves the orthonormal character is parallel transport along the trajectory,

$$\dot{\mathbf{e}}_i=-(V\mathbf{F}+V^{-1}\mathbf{f})\cdot\mathbf{e}_i\mathbf{e}_0. \tag{27}$$

The perturbed trajectory subject to the above conditions then becomes

$$\mathbf{X}'=\mathbf{X}+\sum_i\,\delta X_i\mathbf{e}_i, \tag{28}$$

$$\mathbf{V}'=\mathbf{V}+V^{-1}\sum_i\,\mathbf{f}\cdot\mathbf{e}_i\delta X_i+\sum_i\,\delta V_i\mathbf{e}_i, \tag{29}$$

with equations of motion

$$\frac{d}{dt'}\mathbf{X}'=\mathbf{V}', \tag{30}$$

$$\frac{d}{dt'}\mathbf{V}'=|\mathbf{V}'|^2\mathbf{F}'-\mathbf{F}'\cdot\mathbf{V}'\mathbf{V}'+\mathbf{f}'. \tag{31}$$

Here, $\mathbf{F}'$ and $\mathbf{f}'$ are the values at the perturbed positions, that is,

$$\mathbf{F}'=\mathbf{F}+\sum_i\,\delta X_i\boldsymbol{\nabla}_i\mathbf{F}, \tag{32}$$

$$\mathbf{f}'=\mathbf{f}+\sum_i\,\delta X_i\boldsymbol{\nabla}_i\mathbf{f}. \tag{33}$$

Substituting Eqs. (28), (29), (32), and (33) into Eqs. (30) and (31), ignoring quadratic perturbations, simplifying with the help of Eqs. (14), (15), and (25)–(27), and taking components in the directions of $\mathbf{e}_0$ and the $\mathbf{e}_i$ leads to $6N+2$ equations. One of these is not independent of the others, due to energy conservation. One relates t' and t, and the remaining $6N$ determine the evolution of the perturbations:

$$\frac{dt}{dt'}=1+\sum_i\,(\mathbf{F}+2V^{-2}\mathbf{f})\cdot\mathbf{e}_i\delta X_i, \tag{34}$$

$$\delta\dot{X}_i=\delta V_i, \tag{35}$$

$$\delta\dot{V}_i=\sum_j\,\delta X_j\mathbf{e}_j\cdot(V^2\boldsymbol{\nabla}\mathbf{F}+\boldsymbol{\nabla}\mathbf{f}-V^2\mathbf{F}\mathbf{F}-3V^{-2}\mathbf{f}\mathbf{f}-\mathbf{F}\mathbf{f}-\mathbf{f}\mathbf{F})\cdot\mathbf{e}_i$$
$$-V\mathbf{F}\cdot\mathbf{e}_0\delta V_i. \tag{36}$$

Note that $V\mathbf{F}\cdot\mathbf{e}_0$ is simply ζ, and the terms containing gradients of forces are symmetric, since **F** and **f** are derived from potentials. From these equations, the infinitesimal evolution matrix T for the restricted $6N$ dimensional space may be read off as

$$T=\begin{pmatrix} 0 & I \\ M & -\zeta I \end{pmatrix}, \tag{37}$$

where each of the elements are $3N\times 3N$ submatrices. M is symmetric because **F** and **f** have been derived from a potential, and 0 and I are the zero and unit matrices, respectively. T satisfies the equation

$$T^T J + JT = -\zeta J, \tag{38}$$

where J is given by

$$J=\begin{pmatrix} 0 & I \\ -I & 0 \end{pmatrix}. \tag{39}$$

From this point the analysis is exactly the same as Ref. [21]. Equation (38) leads to similar relations for L and $L^T L$, and hence the eigenvalues of Λ. The end result is that for each exponent λ, $C-\lambda$ is also an exponent, with

$$C=-\langle\zeta\rangle_t, \tag{40}$$

that is, minus the time average of ζ. Thus the conjugate pairing rule holds in the $(\mathbf{q},\sigma,\mathbf{p},\zeta)$ variables, with the exception of the two zero exponents. As noted before, none of the equations of motion depend on σ, so that, omitting the σ equation gives the same exponents (which pair, as shown above), with only one zero exponent.

Conjugate pairing has now been shown for Gaussian and Nosé-Hoover thermostats which act on the kinetic energy. Numerical simulations [24] suggest that the conjugate pairing rule holds also for Gaussian thermostats which keep the internal energy (rather than the kinetic energy) constant.

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