

Time-dependent generalization of the Nosé-Hoover thermostating technique for molecular dynamics simulations

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Abstract. The Nosé-Hoover scheme demonstrates that molecular dynamics simulations can be used to calculate the properties of systems at constant temperature (i.e. canonical ensemble averages). There is interest in deterministic generalizations of Nosé-Hoover dynamics which are ergodic even for simple systems like the harmonic oscillator. Prompted by parallels with studies of the Duffing oscillator within control theory, we have investigated a non-autonomous version of the Nosé-Hoover oscillator in which the temperature is replaced by a weakly time-dependent function. This function is chosen so that its average over time coincides with the temperature desired. Calculations are facilitated by graphical programming with a MATLAB-Simulink platform. A time series analysis of our simple non-autonomous system yields the position and momentum distributions expected for the harmonic oscillator.

1. Introduction

Use of Nosé-Hoover dynamics [1, 2] is an ingenious and simple way of computing canonical ensemble averages within molecular dynamics simulations. For a single one-dimensional harmonic oscillator (of unit mass and angular frequency), the Nosé-Hoover equations of motion are

$$\dot{q} = p, \quad \dot{p} = -q - \frac{p_\eta}{Q} p, \quad \dot{\eta} = \frac{p_\eta}{Q}, \quad \dot{p}_\eta = p^2 - T \quad (1)$$

where q (p) is the oscillator coordinate (momentum), η (p_η) is the coordinate (momentum) of the thermostat and T is the temperature in units such that the Boltzmann constant $k_B = 1$. (For simplicity, we shall, henceforth, set the thermostat mass $Q = 1$.) Ergodicity of the dynamics is essential to the success of the Nosé-Hoover method, i.e. the average over a trajectory must be equal to the average over the full phase space (which includes the thermostat variables). Unfortunately, the system corresponding to equation (1) is not ergodic (see [3] and references therein).

The example of the Nosé-Hoover thermostat and its limitations has spurred the development of several other deterministic thermostating schemes [4-9]. The success of *deterministic* thermostats is, nevertheless, a little surprising. A more plausible approach to the coupling between a system and a thermostat (or heat-bath) is to treat it as *stochastic*. Elimination of the heat-bath degrees of freedom (via Mori-Zwanzig projection [10]) then gives rise to equations of motion for the system's degrees of freedom which are generalized Langevin equations. These equations of motion feature: (i) the replacement, in principle, of the forces within the system by effective forces which include small time-dependent interactions mediated by the heat-bath; (ii) non-Markovian frictional forces which account



for the loss of energy by the system to the heat-bath, and; (iii) random forces (with vanishing average) which are responsible for the transfer of energy from the heat-bath to the system. An explicit realization of generalized Langevin equations (obtained by a careful and transparent derivation) can be found in [11] (see also [12]).

It would be nice to establish a bridge between deterministic thermostats on the one hand and the stochastic description of heat-baths on the other. A pragmatic response to this dichotomy has been to construct hybrid models in which a previously deterministic thermostat is subjected to random forces [13]. Significant improvements in sampling have been reported.

A different perspective entails using the physics of the stochastic description (such as the qualitative features of the generalized Langevin equation discussed above) as a guide in writing down the equations of motion for deterministic thermostats. It is in this spirit that we have experimented with a time-dependent generalization of the Nosé-Hoover thermostat for the harmonic oscillator. It is also the rationale behind the configurational thermostats of [14].

2. A time-dependent Nosé-Hoover thermostat

Within the Nosé-Hoover scheme for the harmonic oscillator [see equation (1)], just one interaction, namely the term $-p_\eta p$ in the equation for \dot{p} , causes the transfer of energy to and from the heat-bath. As we noted above, stochastic models possess independent mechanisms for these two transfers. In casting about for an additional device for energy-transfer, our aim is to retain as far as possible the simplicity of the Nosé-Hoover model. An option compatible with these considerations is to replace the temperature T in the equation for \dot{p}_η by a weakly time-dependent temperature:

$$T \Rightarrow \tau(t) = T[1 + g(t)] \quad (2)$$

It is natural to suppose that changes in the energy of the system would be associated with fluctuations in the temperature τ . Experience with the Duffing oscillator [15] suggests that it will be possible to control the dynamics of the present system with an appropriately chosen “driving term” $g(t)$. Provided the average of g over time vanishes, the average of p^2 over a trajectory will tend to the desired limit of T for large times. This assertion can be proved, under the assumption that p_η is bounded (which is consistent with the results of our numerical simulations), by integrating the modified equation for \dot{p}_η . In this study, we set $g(t) = \varepsilon \sin(\omega_T t)$ and explore the effect of different choices of the positive parameters $\varepsilon (< 1)$ and $\omega_T (\ll \omega = 1)$.

Many numerical techniques have been reported in the literature to solve equation (1) and its variants, among them a second order operator splitting technique [3], the second order velocity Verlet integrator method [4], and the fourth order Hamming’s predictor-corrector algorithm [16].

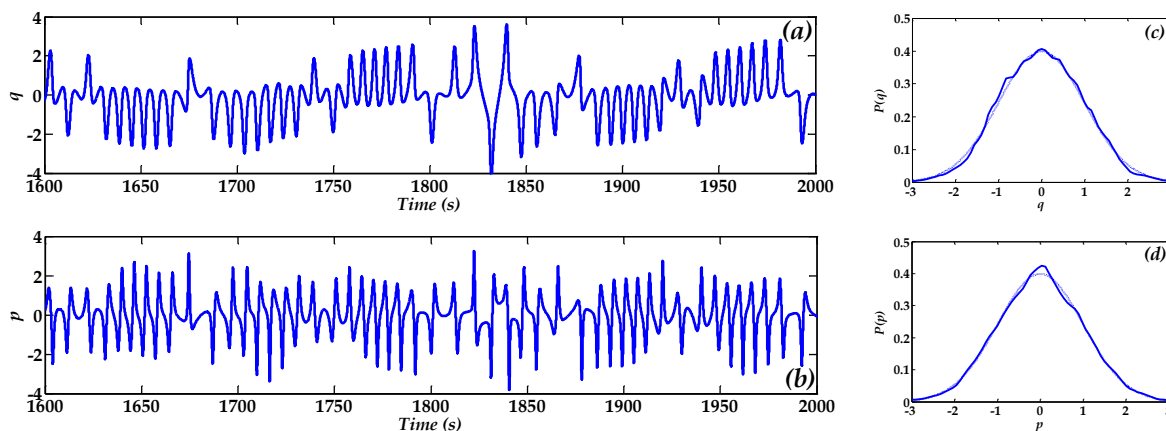


Figure 1. The displacement and momentum of a harmonic oscillator coupled to our time dependent Nosé-Hoover thermostat are shown in (a) and (b), respectively [$q(0) = p(0) = p_\eta(0) = 1$]. The corresponding distribution functions (solid line) are plotted in (c) and (d), respectively, superimposed on the exact equilibrium distributions (dotted line).

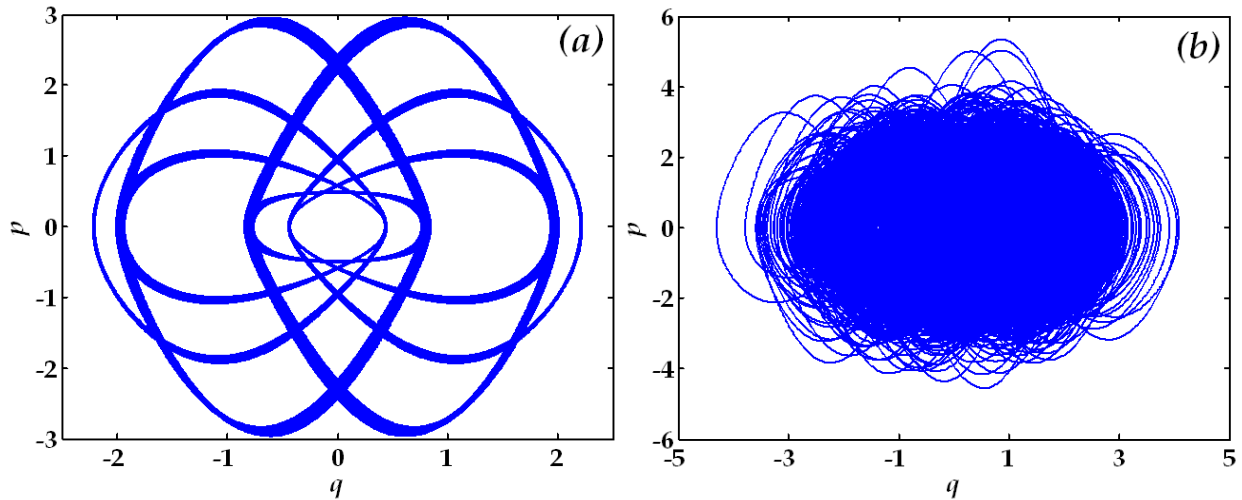


Figure 2. Phase space trajectories for the original and the modified Nosé-Hoover models in (a) and (b), respectively. The initial conditions are $q(0) = 2.2$ and $p(0) = p_\eta(0) = 0$ as in [3].

In this paper, we use Heun's second order integration algorithm with an integration step of 0.005 s, error tolerance of 10^{-14} and a total simulation time of 10,000 s. This algorithm is a two-stage Runge-Kutta method that can be easily implemented within a MATLAB-Simulink environment. To ensure accuracy, a MATLAB script and a graphical Simulink model were run in parallel to reproduce the results reported in [4].

The typical choice of $\tau(t) = 1 + 0.5\sin(0.1t)$ for the modified Nosé-Hoover thermostat results in figure 1, which shows the system is unstable but bounded. In addition, the distribution functions are seen to be very close to the Gaussian distributions expected for an ergodic system. Decreasing ω_T below 0.1, while keeping $\varepsilon = 0.5$, one finds non-ergodic behaviour with negligible effect on the dominant frequency of the system. If, instead, one decreases ε below 0.5, with $\omega_T = 0.5$, the dynamics is quite similar to that of the original Nosé-Hoover system [equation (1)], indicating loss of sensitivity to the time-dependent perturbation in equation (2). The robustness of the (apparent) ergodic behaviour of the modified Nosé-Hoover model for other choices of initial conditions is illustrated in figure 2 for the same case reported in [3] (which deals with the original Nosé-Hoover model).

Phase space trajectories for the original and the modified Nosé-Hoover models are plotted in figure 3, along with the power spectra of the displacements. Our results agree with those reported in the literature for the dominant frequency when $Q = 1$ (small thermostat mass). The power spectrum of the modified system is non-trivial and qualitatively similar to that found for hyperchaotic high-order oscillators, whereas the power spectrum of the unmodified Nosé-Hoover oscillator has a single *super*-dominant frequency (reflecting the torus-like shape of its strange attractor). It is reasonable to infer that the perturbation due to the forcing function *seems to be sufficient to produce an ergodic system with just one thermostat*. By contrast, two or more *chained* thermostats were required in [4].

3. Discussion

The work reported here is at a preliminary stage. Our results are encouraging. A harmonic oscillator coupled to a weakly *time-dependent* Nosé-Hoover thermostat does seem to be ergodic, which is, perhaps, not unexpected: the Hamiltonian-like function $H = \frac{1}{2}(p^2 + q^2 + p_\eta^2) + \eta T$ loses its status as a constant of the motion when T is replaced by $\tau(t)$ in equation (2). (One finds that $\dot{H} = \eta T \dot{g}$.) However, our modification of the Nosé-Hoover thermostat does have one potentially serious drawback. The equilibrium distribution function $f_{eq} \propto \exp[-(p^2 + q^2 + p_\eta^2)/2T]$ does not belong to the kernel of the Liouvillian operator L for our modified Nosé-Hoover model. Instead,

$$Lf_{eq} = g(t)p_\eta f_{eq} \quad (3)$$

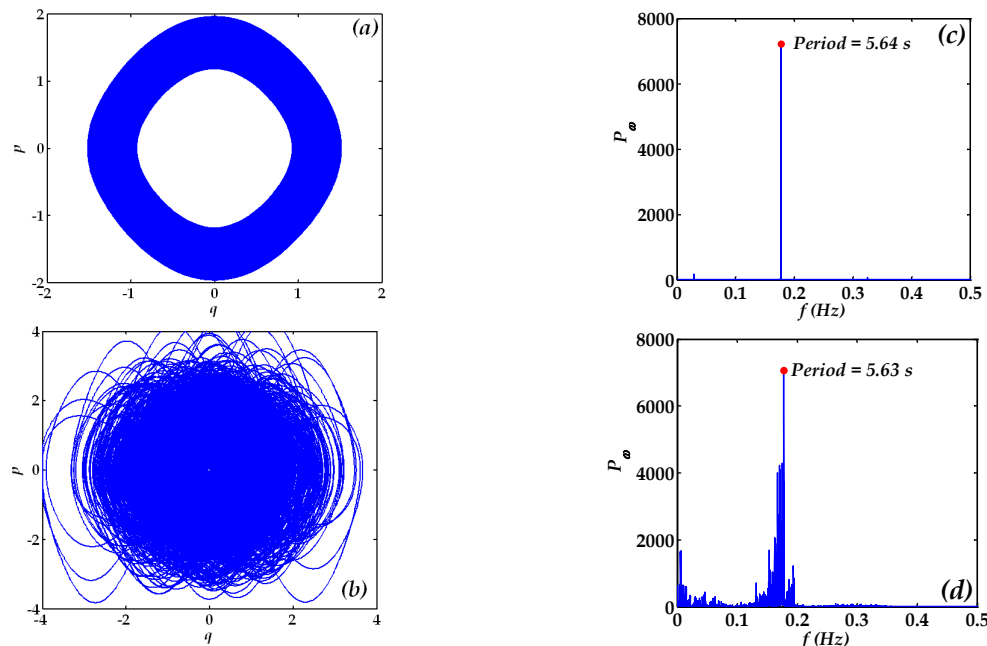


Figure 3. Phase space trajectories of the harmonic oscillator coupled to the original and to the time-dependent Nosé-Hoover thermostat are plotted in (a) and (b), respectively. The corresponding power spectra of the displacement $q(t)$ are shown in (c) and (d), respectively. These indicate that, while the original Nosé-Hoover system is regular, the modified system appears to be not only ergodic but also chaotic.

[Actually, the result in equation (3) is independent of the choice of potential $V(q)$.] Nevertheless, the distributions we have generated to date (examples of which are given in figure 1) are not manifestly inconsistent with the exact equilibrium distributions, which may be a consequence of the fact that the right-hand side of equation (3) is, by design, a small oscillating function of time with vanishing average. Perhaps, it is sufficient if Lf_{eq} is zero on average, i.e.

$$\lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t Lf_{eq} dt' = 0 \quad (4)$$

Clearly, this issue merits further careful investigation.

4. References

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