A Hamiltonian Formulation for Recursive Multiple Thermostats in a Common Timescale.

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Abstract

Molecular dynamics trajectories that sample from a Gibbs distribution can be generated by introducing a modified Hamiltonian with additional degrees of freedom as described by Nosé [S.Nosé, Mol. Phys., 52, 255, 1984]. To achieve the ergodicity required for canonical sampling, a number of techniques have been proposed based on incorporating additional thermostating variables, such as Nosé-Hoover chains and more recent fully Hamiltonian generalizations. For Nosé dynamics, it is often stated that the system is driven to equilibrium through a resonant interaction between the self-oscillation frequency of the thermostat variable and a natural frequency of the underlying system. In this article, we clarify this perspective, using harmonic models, and exhibit practical deficiencies of the standard Nosé-chain approach. As a consequence of our analysis, we propose a new powerful “recursive thermostating” procedure which obtains canonical sampling without the stability problems encountered with Nosé-Hoover and Nosé-Poincaré chains.

keywords: Nosé, Nosé-Hoover, Nosé-Poincaré, Nosé-Poincaré Chains, symplectic integrator, constant temperature molecular dynamics, thermostating.

1 Introduction

The desire to provide computer simulation of molecular dynamics which samples from the canonical ensemble has led to the extensive use of momentum scaling methods to regulate the kinetic energy, and hence temperature, of the system. This is accomplished by introducing additional degrees of freedom which interact with the original system in some manner to simulate a heat
bath. Most of the methods in use have their roots in the work of Andersen in [1] where constant pressure and temperature were considered. The paper of Nosé [9] constructed a family of extended dynamical systems, for which it can be shown analytically that sampling from the canonical ensemble occurs under an ergodicity assumption. For an \( N \)-body system, with original Hamiltonian \( H(q, p) \), the construction was based on one additional degree of freedom with an extended Hamiltonian,

\[
H_N(q, s, p, p_s) = H\left(q, \frac{p}{s}\right) + \frac{p_s^2}{2Q} + (N + 1)kT \ln s,
\]

(1)

where \( s \) is the new thermostating variable, \( p_s \) the corresponding momentum, \( T \) is temperature, \( Q \) the Nosé mass and \( k \) is the Boltzmann constant. There exist many variations of these schemes in the literature, but fundamental deficiencies have limited their use compared to alternatives, such as stochastic methods.

Nosé’s method introduces an artificial scaling of the time variable which makes computation of time-correlation functions cumbersome. While correcting this deficiency, Hoover’s coordinate and time transformations [4] destroy the Hamiltonian structure. To produce Hoover’s method for an underlying Hamiltonian of the form,

\[
H(q, p) = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(q),
\]

(2)

both time and coordinate transformations are applied to (1) \((p' = p/s, t' = \int dt/s, \pi'_{s} = \pi_{s}/s, \zeta = (1/s)ds/dt' = s \pi'_{s}/Q, \eta = \ln s)\) to give,

\[
\frac{dq_i}{dt'} = \frac{p'_{i}}{m_i}, \quad \frac{dp'_{i}}{dt'} = -\nabla q_i V(q) - \zeta p'_{i},
\]

\[
\frac{d\eta}{dt'} = \zeta, \quad \frac{d\xi}{dt'} = \frac{1}{Q} \left( \sum_{i=1}^{N} \frac{p^{'2}_{i}}{m_i} - NkT \right).
\]

More recent work by Bond, Leimkuhler and Laird in [3] introduced the Nosé-Poincaré method wherein the desired rescaling of time is accomplished through transformation of the Hamiltonian itself,

\[
H_{NP}(q, s, p, p_s) = s \left( H\left(q, \frac{p}{s}\right) + \frac{p_s^2}{2Q} + NkT \ln s - H_0 \right).
\]

(3)

Here \( N \) is the number of degrees of freedom of the real system, and \( H_0 \) is chosen such that the Nosé-Poincaré Hamiltonian, \( H_{NP} \), is zero when evaluated at initial conditions. A symplectic numerical method is included in [3] and further research on integrators and applications [6, 10, 7] has helped to establish the Nosé-Poincaré framework.

A feature associated with these methods is the introduction of a parameter, \( Q \), the Nosé mass. The selection of this mass is critical if the correct sampling is
to be obtained, and it is generally calculated so that the auxiliary variable has
a self-resonant frequency, estimated by linearizing the system, coincident with
some natural frequency within the original system. Thermostatting chains, such
as Nosé-Hoover chains in [8] and Nosé-Poincaré chains [2], were introduced to
generate the correct sampling for small and stiff systems, for which Nosé-Hoover
and Nosé-Poincaré dynamics are not ergodic, by using additional degrees of
freedom. It is noted that, for these methods, the choice of the Nosé mass
for the first thermostat is less critical than in Nosé, Nosé-Hoover and Nosé-
Poincaré methods. However the stability of the numerical implementation of
Nosé-Poincaré chains is not as good as the underlying Nosé-Poincaré method
as each additional thermostat controls only one other thermostat, and this is
analogous to thermostatting a low dimensional system such as the harmonic
oscillator. We have seen that, for the harmonic oscillator, Nosé’s method has
poor stability when compared to time reparametrization methods due to the
artificial scaling of time introducing large time steps when the dynamics of the
underlying oscillator is subject to the greatest rate of change. Each additional
thermostat sub-system will have this problem as the time reparametrization
is only based on the first thermostat. In addition the low dimension of the
sub-system to be thermostatted means that the expected average values for
quantities based on the thermostating variable’s momentum may not be easily
achievable, as observed in Section 4.2, and to overcome this several additional
thermostats are required. These problems persist regardless of the dimension of
the underlying system.

In this article we develop a more general class of recursive momentum-
scaling multiple thermostat (RMT) methods. Extensive computer experimenta-
tion with these formulations has shown that a seemingly natural approach
to parameter selection based on a simple linearization of the underlying dy-
namics leads to an incorrect choice of parameters. In fact, we find that the
parameters (thermostat masses) in our formulation are essentially independent
of the underlying system. This observation has very important advantages for
the development of practical numerical approaches. The new method presented
here can be applied more easily to thermostat a variety of models without the
need for tedious tuning of parameters. The parameters can instead be chosen to
obtain some useful property in the numerical method, such as better numerical
stability or, as in [11] a desired scale separation.

To gain a better understanding of the basic methods we examine the role of
the Nosé mass in providing ergodic behavior in Section 2. In Section 3, a gen-
eral momentum scaling Hamiltonian formulation is introduced and we describe
as special cases the Nosé-Poincaré chains method [2] and the Recursive Multi-
ple Thermostat (RMT) method. The RMT is a real-time Hamiltonian method
having Nosé masses which are independent of the natural frequencies of the
underlying dynamical system. A summary of the results of this paper is then
discussed in Section 5. An important feature of our formalism is that we remain
always within the class of Hamiltonian dynamical models, for which symplectic
integrators, having superior long-term stability properties, are possible. Con-
struction of efficient schemes suitable for molecular dynamics applications is an important task. In Appendix A we show that this is possible in our case, by designing an efficient Hamiltonian splitting method for RMTs.

An electronic aid to understanding the thermostatting methods described in this article is available at the URL http://www.recursivethermostat.info.

2 Analysis of the Nosé-Poincaré Method.

In this section we analyze the behavior of the real time Nosé-Poincaré method when applied to a single harmonic oscillator. By examining the auxiliary variable phase-space and modelling the system in the frequency domain we provide a better understanding of the role of the Nosé mass parameter. We anticipate that a very similar analysis would apply to Nosé-Hoover dynamics.

2.1 Auxiliary Variable Phase-Space.

If we consider the classical N-body problem (2) with potential bounded below, \( V(q) \geq 0 \ \forall q \), and apply a thermostat using the Nosé-Poincaré method (3) we can see that, for initial energy \( E = H_0 \),

\[
\frac{p^2}{2Q} + NkT \ln s \leq E,
\]

and hence the phase-space of the auxiliary variables is bounded by the equation,

\[
s = \exp\left(\frac{E - \frac{p^2}{2Q}}{NkT}\right).
\]

We consider a harmonic oscillator with underlying energy \( H(q,p) = q^2/2 + p^2/2 \), thermostatted using the Nosé-Poincaré method, and examine, in Figure 1, the effect of a change in the Nosé mass on the auxiliary variable phase space. The parameters used were \( E = 1, kT = 1 \) and \( \omega = 1 \) for \( Q = 0.3, Q = 0.5 \) and \( Q = 2 \). As \( Q \) is reduced the phase-space occupied by the auxiliary variables (dots) increases and the bounding curve (solid line), given by (5), decreases. At \( Q \approx 0.3 \) the auxiliary variables reach the boundary and, at this point, although the system is not sufficiently ergodic to produce sampling from the canonical ensemble, the results are close in some sense as shown in Figure 2. From Nosé’s linearized equation in [9], \( Q = 2gkT/\omega \), we would expect that the optimum \( Q = 2 \) whereas in practice we see that at this value the system is sampling from the microcanonical ensemble. Since the oscillator is started at the correct temperature we expect that the average value of \( s \) will be 1 (as shown in Section 2.1).
In Figure 3 the relationship between the mean thermostat kinetic energy $\langle p_s^2/Q \rangle$ and $Q$ is shown for $Q$ in the range 0.001-2. $\langle p_s^2/Q \rangle$ peaks after the point where the auxiliary variables reach the boundary of their phase-space, as given in (5), at a value of approximately $kT$.

### 2.2 Average Values for the Auxiliary Variables.

As shown in Section 2.1, $\langle p_s^2/Q \rangle$ peaks at the optimum value for the Nosé mass $Q$. It is possible to calculate the average values for both the quantity $p_s^2/Q$ and the auxiliary variable, $s$, if we assume that the system is ergodic.

\[ Q = 2.0, Q = 0.5, Q = 0.3 \]

Figure 1: Auxiliary variable phase-space with $Q=2.0$, $Q=0.5$ and $Q=0.3$.

\[ Q = 2.0, Q = 0.3 \]

Figure 2: Harmonic oscillator $q, p$ distributions with $Q=2$ and $Q=0.3$.

\[ Q = 2.0, Q = 0.3 \]

In [5] introducing ergodicity by coupling a box of soft spheres into the thermostating momentum resulted in the correct distributions, but only where $Q < NkT/(2\omega Q)$, corresponding to $Q < 0.5$ in the above example.
Figure 3: \( \langle p_s^2/Q \rangle \) for \( Q \) in the range 0.001-2 with values of \( Q \) for \( \langle p_s^2/Q \rangle > 1 \) (thick dashed) and Nosé’s estimate (thick dots).

We consider the Nosé-Poincaré method (3) where it is possible to obtain real-time results without sacrificing the symplectic structure by using a Poincaré transformation.

**Theorem 2.1** When thermostatting with the Nosé-Poincaré method (3), if the system is ergodic, then the average of the auxiliary variable, \( s \), will be given by,

\[
\langle s \rangle = \exp \left( \frac{H_0}{NkT} \right) \left( \frac{N}{N + 1} \right)^{\frac{2N+1}{2}}.
\]

**Proof** For an ergodic system the average of \( s \) is,

\[
\langle s \rangle = \frac{\int dp_s \int ds \int dp \int dq s \delta [H_{NP} - 0]}{\int dp_s \int ds \int dp \int dq \delta [H_{NP} - 0]}.
\]

Substituting (3) into the numerator of (7) we get,

\[
\int dp_s \int ds \int d\tilde{p} \int dq s \delta \left[ \left( H(q, \frac{p}{s}) + \frac{p_s^2}{2Q} + NkT \ln s - H_0 \right) \right].
\]

We can substitute \( \tilde{p} = p/s \), the volume element then becomes \( dp = s^N d\tilde{p} \). There is no upper limit in momentum space so we can change the order of integration of \( dp \) and \( ds \) giving,

\[
\int dp_s \int d\tilde{p} \int dq \int ds s^{N+1} \delta \left[ \left( H(q, \tilde{p}) + \frac{p_s^2}{2Q} + NkT \ln s - H_0 \right) \right] s.
\]
Whenever a smooth function, \( g(s) \), has a single simple root at \( s = s_0 \) we can write the equivalence relation for \( \delta \), \( \delta[g(s)] = \delta[s - s_0]/|g'(s_0)| \), then,

\[
\frac{1}{NkT} \delta \left[ \frac{H(q, \tilde{p}) + \frac{p_s^2}{2Q} + NkT \ln s - H_0}{NkT} \right] = \delta \left[ s - \exp \left( -\frac{1}{NkT} \left( H(q, \tilde{p}) + \frac{p_s^2}{2Q} - H_0 \right) \right) \right].
\]

Substituting (10) into (9) and using the sifting property of \( \delta \) we get,

\[
\frac{1}{NkT} \int dp_s \int d\tilde{p} \int dq \exp \left( -\frac{(N + 1)}{NkT} \left( H(q, \tilde{p}) + \frac{p_s^2}{2Q} - H_0 \right) \right).
\]

Rescaling \( \tilde{p} = \tilde{p} \sqrt{N+1} \), \( \tilde{q} = q \sqrt{N+1} \) and \( \tilde{p}_s = p_s \sqrt{N+1} \) in (11),

\[
C_1 \int d\tilde{p}_s \int d\tilde{p} \int d\tilde{q} \exp \left( -\frac{1}{NkT} \left( H(\tilde{q}, \tilde{p}) + \frac{\tilde{p}_s^2}{2Q} \right) \right),
\]

where,

\[
C_1 = \frac{1}{(N + 1)^{\frac{N-1}{2}}} NkT \exp \left( \frac{(N + 1)H_0}{NkT} \right).
\]

Similarly we can substitute \( \tilde{p} = p/s \) into the denominator of (7), use the equivalence relation for \( \delta \) and define \( \tilde{p} = \tilde{p} \sqrt{N} \), \( \tilde{q} = q \sqrt{N} \) and \( \tilde{p}_s = p_s \sqrt{N} \) to get,

\[
C_2 \int d\tilde{p}_s \int d\tilde{p} \int d\tilde{q} \exp \left( -\frac{1}{NkT} \left( H(\tilde{q}, \tilde{p}) + \frac{\tilde{p}_s^2}{2Q} \right) \right),
\]

where,

\[
C_2 = \frac{1}{N^\frac{N-1}{2}} NkT \exp \left( \frac{NH_0}{NkT} \right).
\]

Substituting (12) and (13) into (7) we get (6) as required.

We note that \( \exp(x) = \lim_{n \to \infty} (1 + x/n)^n \). Then, in the limit \( N \to \infty \),

\[
\langle s \rangle = \exp \left( \frac{H_0}{NkT} - 1 \right).
\]

Substituting \( N = 1 \) into (6) gives \( \langle s \rangle = \exp(H_0/kT - 0.96) \), a result close to (14). From this we conclude that (14) is a good approximation of \( \langle s \rangle \) for all \( N \).

We also have,
**Theorem 2.2** When thermostatting with the Nosé-Poncaré method (3), if the system is ergodic, then the average of the quantity \( p_s^2/Q \), will be given by,

\[
\left\langle \frac{p_s^2}{Q} \right\rangle = kT.
\]

**Proof** If the system is ergodic, then the average of \( p_s^2/Q \) will be given by substituting \( p_s^2/Q \) for \( s \) in (7). In a method similar to that used above we can substitute \( \tilde{p} = p/s \) and use the equivalence relation for \( \delta \) in both the denominator and numerator of the new equation. Noting that,

\[
\int_{-\infty}^{\infty} \frac{p_s^2}{Q} \exp \left( -\frac{p_s^2}{2QkT} \right) dp_s = kT \int_{-\infty}^{\infty} \exp \left( -\frac{p_s^2}{2QkT} \right) dp_s,
\]

the new equation reduces to (15).

\[\square\]

2.3 Frequency Domain Model of the Nosé-Poincaré method.

We would like to analyze Nosé’s method to determine the optimum value of \( Q \) but, despite it’s apparent simplicity, Nosé’s method it is difficult to analyze dynamically. An alternative approach is to model the method in the frequency domain, and to do this it is necessary to use a method where the dynamics are in real time such as the Nosé-Poincaré method. By modelling the system for \( Q \) greater than it’s “optimum value”, the value of \( Q \) at which the auxiliary variables intersect the boundary of their phase-space can be determined.

Consider a system with a Hamiltonian,

\[
H_N(q, p) = \frac{p^2}{2m} + \frac{q^2}{2}.
\]

The corresponding Nosé-Poincaré Hamiltonian is given by (3). We will assume that the fundamental frequency of the modified system is unchanged at \( \omega = m^{-\frac{3}{2}} \) and that all other frequencies in \( p/s \) and \( q \) are of sufficiently small magnitude to be ignored. In addition we will assume that time averages of time derivatives vanish i.e. for \( x(t) \) and time \( T \),

\[
\langle \dot{x}(t) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T \dot{x}(t) \, dt = \lim_{T \to \infty} \left( \frac{x(T) - x(0)}{T} \right) = 0.
\]

We can determine the average value of the oscillator kinetic term by considering the equations of motion for \( p_s \),

\[
\dot{p}_s = -\frac{\partial H_{NP}}{\partial s} = \frac{\tilde{p}^2}{m} - kT,
\]

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where \( \tilde{p} = p/s \). Taking averages, and using our second assumption gives,

\[
\left\langle \frac{\tilde{p}^2}{m} \right\rangle = kT, \tag{20}
\]

These assumptions, and the predicted average kinetic energy, are generally observed in experiments.

We consider a harmonic oscillation and study the corresponding driven dynamics of the \( s, p_s \) variables. A harmonic vibration with average kinetic energy \( kT \) and frequency \( \omega \) takes the form,

\[
\tilde{p} = \sqrt{2mkT} \cos(\omega t). \tag{21}
\]

From the equation of motion for \( q \),

\[
\dot{q} = -\frac{\partial H_{NP}}{\partial p} = \frac{sp_s}{ms^2} = \frac{\tilde{p}}{m}, \tag{22}
\]

we get,

\[
q = \sqrt{2kT} \sin(\omega t), \tag{23}
\]

the constant of integration being zero for the harmonic oscillator.

These equations, together with the equations of motion, can then be used to solve for \( p_s \) and \( s \). From the equations of motion for \( p_s \),

\[
\dot{p}_s = -\frac{\partial H_{NP}}{\partial s} = \frac{\tilde{p}^2}{m} - kT = \frac{2mkT \cos^2(\omega t)}{m} - kT = kT \cos(2\omega t), \tag{24}
\]

integrating with respect to \( t \),

\[
p_s = \int kT \cos(2\omega t) \, dt = \frac{kT \sin(2\omega t)}{2\omega} + C_1, \tag{25}
\]

where \( C_1 \) is a constant, which can be determined as follows. From the equations of motion for \( s \),

\[
\dot{s} = \frac{\partial H_{NP}}{\partial p_s} = \frac{sp_s}{Q}, \tag{26}
\]

which can be re-arranged as,

\[
\frac{Q\dot{s}}{s} = p_s. \tag{27}
\]

From this we can see that \( p_s \) is a time derivative and has an average of zero,

\[
\left\langle p_s \right\rangle = \left\langle \frac{Q\dot{s}}{s} \right\rangle = Q \left\langle \frac{d\ln s}{dt} \right\rangle = 0, \tag{28}
\]

from our second assumption. Hence \( C_1 = 0 \) giving,

\[
p_s = \frac{kT \sin(2\omega t)}{2\omega}. \tag{29}
\]
Figure 4: Frequency domain plot with $Q=2.0$. $\tilde{p}$ has a fundamental frequency of 0.167Hz as expected, and $p_s$ has a fundamental frequency (at the $1^{st}$ harmonic) of 0.334Hz, as predicted in (29).

To obtain an expression for $s$ we integrate both sides of (27) with respect to $t$ to get,

$$Q \ln s = -\frac{kT \cos(2\omega t)}{4\omega^2} + C_2,$$

for constant $C_2$. Hence,

$$s = C_3 \exp \left( -\frac{kT \cos(2\omega t)}{4Q\omega^2} \right),$$

where $C_3$ is a constant such that $\langle s \rangle$ satisfies (14). We can then show that,

$$s = A \exp \left( \frac{H_0}{kT} - 1 \right) \exp \left( -\frac{kT \cos(2\omega t)}{4Q\omega^2} \right),$$

where,

$$A = \left\langle \exp \left( -\frac{kT \cos(2\omega t)}{4Q\omega^2} \right) \right\rangle^{-1}.$$

There is strong experimental evidence in support of this model when $Q$ is greater than its optimum value. Figure 4 shows the Fourier analysis of a harmonic oscillator, with $kT = 1$, $\omega = 1$ and $Q = 2$, for $\tilde{p}$ and $p_s$. We note that $\tilde{p}$ has a fundamental frequency of 0.167Hz as expected, and $p_s$ has a fundamental frequency (at the $1^{st}$ harmonic) of 0.334Hz as predicted by the model.

If we consider the quantity,

$$\langle |p_s| \rangle = \left\langle \left| \frac{kT \sin(2\omega t)}{2\omega} \right| \right\rangle = \sqrt{2}kT,$$

(34)
Table 1: Average values for $|p_s|$ with varying $Q$ and $\omega$.

| $\omega$ | $Q$ | Actual $\langle |p_s| \rangle$ | Model $\langle |p_s| \rangle$ |
|----------|-----|-------------------------------|-----------------------------|
| 1        | .5  | .349                          | .354                        |
| 1        | 1   | .361                          | .354                        |
| $\sqrt{2}$ | 1   | .493                          | .501                        |
| $\sqrt{2}$ | 2   | .510                          | .501                        |

2.4 Estimating the Nosé Mass.

The model can be used to estimate the Nosé mass by calculating where the phase-space area occupied by the auxiliary variables interacts with the phase-space boundary, as shown in Section 2.1. For large $Q$ we see that, from both Figure 1 and the model in the proceeding section (29)-(32), the maximum value of $p_s$ occurs at the average value of $s$. Since the auxiliary variables phase-space is bounded by (5) substituting the average value of $s$, given by (14), has solutions for $p_s^*$, the value of $p_s$ at the phase-space boundary,

$$p_s^* = \sqrt{2QkT},$$

(35)

for the single harmonic oscillator ($N = 1$). To estimate the maximum value for $p_s$ when $s = \langle s \rangle$ we will assume that $p_s$ is scaled by some factor $a \geq 1$. Scaling (29) and following the methods in Section 2.3 yields the following equations for the scaled auxiliary variables,

$$p_s = \frac{akT \sin(2\omega t)}{2\omega},$$

(36)

and,

$$s = A_a \exp \left( \frac{H_0}{kT} - 1 \right) \exp \left( -\frac{akT \cos(2\omega t)}{4Q\omega^2} \right),$$

(37)

where,

$$A_a = \left\langle \exp \left( -\frac{akT \cos(2\omega t)}{4Q\omega^2} \right) \right\rangle^{-1}.$$  

(38)

While the phase-space occupied by the auxiliary variables does not interact with the boundary some energy, say $E_r$, is retained by the system at all times and, from (5), the auxiliary variable phase-space is bounded by,

$$\frac{p_s^2}{2Q} + kT \ln s = E - E_r.$$  

(39)
Substituting (36) and (37) into (39),

\[
\frac{a^2(kT)^2 \sin^2(2\omega t)}{8Q\omega^2} + kT \ln A_a + E + kT - \frac{a(kT)^2 \cos(2\omega t)}{4Q\omega^2} = E - Er. \tag{40}
\]

The \( \frac{p_s^2}{2Q} \) term has maxima at \( t = \pi/4\omega, 3\pi/4\omega, \cdots \) where the \( \ln s \) term is at its average value and, conversely, the \( \ln s \) term has maxima at \( t = \pi/2\omega, 3\pi/2\omega, \cdots \) where \( \frac{p_s^2}{2Q} = 0 \).

From the model, where \( a = 1 \), (40) gives,

\[
\max \left( \frac{p_s^2}{2Q} \right) < \max \left( kT \ln s \right). \tag{41}
\]

As \( a \) is increased \( \max \left( \frac{p_s^2}{2Q} \right) \) increases at a greater rate than \( \max \left( kT \ln s \right) \) until it reaches the limit imposed by (39). The energy at the maximum points is now equal, substituting \( t = \pi/4\omega \) and \( t = \pi/2\omega \) into (40) and equating the results to find \( \hat{a} = \max(a) \),

\[
\frac{\hat{a}^2(kT)^2}{8Q\omega^2} = \frac{\hat{a}(kT)^2}{4Q\omega^2}, \tag{42}
\]

with non-trivial solution,

\[
\max(a) = \hat{a} = 2. \tag{43}
\]

This solution provides an upper bound for \( a \), however examination of the auxiliary variable phase-space trajectories for the model when \( a = 2 \) shows that for most of the trajectory the total energy is greater than \( E - Er \). A more accurate estimate for the upper bound can be found by solving for trajectories with energy not exceeding \( E - Er \), where \( Er \) is defined when \( a = 2 \). Differentiating (40) with respect to \( t \) to find maxima,

\[
\frac{a^2(kT)^2 \sin(2\omega t) \cos(2\omega t)}{2Q\omega} + \frac{a(kT)^2 \sin(2\omega t)}{2Q\omega} = 0, \tag{44}
\]

giving maxima at \( t = \pi/2\omega, 2\pi/\omega, \cdots \) and \( \cos(2\omega t) = -a^{-1} \). Substituting \( \cos(2\omega t) = -a^{-1} \) into (40) for \( \bar{a} = \max(a) < 2 \) gives,

\[
\frac{(\bar{a}^2 - 1)(kT)^2}{8Q\omega^2} + kT \ln A_{\bar{a}} + E + \frac{(kT)^2}{4Q\omega^2} = E - Er, \tag{45}
\]

For this to be within the energy bound imposed by \( a = 2 \) we have,

\[
\frac{(\bar{a}^2 - 1)(kT)^2}{8Q\omega^2} + \frac{(kT)^2}{4Q\omega^2} = \frac{(kT)^2}{2Q\omega^2}, \tag{46}
\]

with solution,

\[
\bar{a} = \sqrt{3} \approx 1.73. \tag{47}
\]
Figure 5: Auxiliary variable phase-space with $Q=2.0$, $Q=1.0$ and $Q=0.5$. Key: Actual phase-space=dots, predicted phase-space=thick solid, phase-space limit $E - E_r$=dashed, phase-space boundary=thin solid.

This result provides the maximum value for $a$ when $\ln s$ is equal to $\langle \ln s \rangle$ and, for large $Q$, is close to $\ln \langle s \rangle$ the point at which we require the maximum value for $p_s$. For smaller $Q$ we need to correct for the additional $\ln A_a$ term. From (39) for $\tilde{a} = \max(a) < \sqrt{3}$,\
\[
\frac{\tilde{a}^2(kT)^2}{8Q\omega^2} = \frac{3(kT)^2}{8Q\omega^2} + kT \ln A_{\tilde{a}},
\]
giving,
\[
\tilde{a} = \sqrt{3 + \frac{8Q\omega^2 \ln A_{\tilde{a}}}{kT}}. \tag{49}
\]
For $Q = 0.5$, $kT = 1$ and $\omega = 1$ we get $\tilde{a} \approx 1.54$.

Figure 5 shows the experimental results for a thermostatted harmonic oscillator where $kT = 1$, $\omega = 1$ and $Q = 0.5, 1.0, 2.0$, the actual measurements are the dots, the predicted phase-space is the thick solid line, the phase-space limit $E - E_r$ is the dashed line and the phase-space boundary is the thin solid line. This indicates that there is good correlation between the results predicted from the model and the actual experiments.

The maximum value of $p_s$ from (47) and (36) is,
\[
\max(p_s) \leq \frac{\tilde{a}kT}{2\omega} \approx \frac{0.87kT}{\omega}. \tag{50}
\]
The auxiliary variables will reach the boundary of phase-space when $\max p_s = p^*_s$ from (35),
\[
Q \leq \frac{0.38kT}{\omega^2}. \tag{51}
\]
This should be compared with Nosé’s estimate in [9] of $Q = 2kT/\omega^2$. For the example of the harmonic oscillator, with $kT = 1$, $\omega = 1$, using the correction in
Table 2: Auxiliary variable self oscillation frequency for small $Q$.

<table>
<thead>
<tr>
<th>$Q$</th>
<th>$\frac{2gkT}{Q}$ (Hz)</th>
<th>Actual (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>3.3</td>
<td>2.8</td>
</tr>
<tr>
<td>0.01</td>
<td>2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>0.02</td>
<td>1.7</td>
<td>1.4</td>
</tr>
</tbody>
</table>

(49) is $Q \approx 0.29$, which compares well with the experimentally obtained value of $Q = 0.3$ as shown in Figure 1.

### 2.5 Behavior of the Nosé-Poincaré method for small $Q$.

For small values of $Q$ it has been observed by Hoover [4] and others that the auxiliary variables will oscillate independently of the system to be thermostatted. Under these conditions, where the frequency of the system is less than that of the auxiliary variable self oscillation frequency, Nosé's assumptions for the oscillation frequency now hold, as can be seen in Table 2 and Figure 6 for a thermostatted harmonic oscillator with $kT = 1, \omega = 1$. Experiments indicate that the onset of self-oscillation is typically around three times the fundamental frequency of the system, giving a very small band for the correct choice of $Q$, as seen in Figure 3. From this Figure we have $\langle p_s^2/Q \rangle \approx 0.8kT$ after the onset of self-oscillation, as $Q$ decreases.

### 2.6 Thermostatting multiple oscillators.

Applying Nosé thermostats to multiple harmonic oscillators can be analyzed in a similar manner to the case of the single harmonic oscillator.

It is generally assumed that the auxiliary variables will only interact with parts of the thermostatted system which have a fundamental frequency near to the self-oscillation frequency of the auxiliary variables. This is not generally the case as can be seen from Figure 7, a Fourier plot of the auxiliary variable when thermostatting 4 oscillators of frequencies $\omega_1 = 1.00, \omega_2 = 0.308, \omega_3 = 0.095$ and $\omega_4 = 0.052$, temperature $kT = 1$ and Nosé mass $Q = 2gkT/\omega_4^2 = 3200$ (which should resonate with oscillator 4). The magnitude of the position components for each oscillator are approximately the same, from (21) the magnitude of the oscillators momentum will be proportional to $\omega^{-1}$ and from (29) the magnitude of the component for each oscillator in the auxiliary variable momentum, $p_s$, will be proportional to an additional $\omega^{-1}$, hence $p_s$ has been scaled by $\omega$. Note that, in this microcanonical experiment, each oscillator is represented by its first harmonic in the auxiliary variable momentum as predicted in the model of
Figure 6: Frequency domain plot of a Nosé-Poincaré thermostatted harmonic oscillator with $\omega = 1$ (0.167Hz), for small values of $Q$.

Section 2.3, and that the interaction with the auxiliary variables is similar for all of the oscillators.

### 2.7 Extension of the model for multiple oscillators.

The model of Section 2.3 can easily be extended to multiple harmonic oscillators. Given a Hamiltonian for $N$ oscillators,

$$
\tilde{H}_N = \sum_{i=1}^{N} \left( \frac{p_{i}^2}{2m_i} + \frac{q_{i}^2}{2} \right).
$$

(52)

The corresponding Nosé-Poincaré Hamiltonian is given in (3). As before we will assume that the fundamental frequencies of the modified system are the same as those in the original system and that all other frequencies are of sufficiently small magnitude to be ignored. In addition we will assume that time averages of time derivatives vanish and that the initial energy is equally distributed between the oscillators. Then,

$$
\left\langle \frac{\tilde{p}_i^2}{m_i} \right\rangle = kT,
$$

(53)

where $\tilde{p}_i = p_i/s$. Following the analysis as before yields,

$$
\tilde{p}_i = \sqrt{2m_i kT \cos(\omega_i t)}, \quad q_i = \sqrt{2kT} \sin(\omega_i t), \quad i = 1, 2, \cdots, N,
$$

(54)

$$
p_s = \sum_{i=0}^{N} \frac{N kT \sin(2\omega_i t)}{2\omega_i},
$$

(55)
Figure 7: Frequency domain plot of position and scaled auxiliary variable momentum for 4 oscillators.

\[ s = \tilde{A} \exp \left( \frac{H_0}{NkT} - 1 \right) \prod_{i=0}^{N} \exp \left( -\frac{kT \cos(2\omega_i t)}{4Q\omega_i^2} \right) \], \quad (56)

where,

\[ \tilde{A} = \left\langle \prod_{i=0}^{N} \exp \left( -\frac{kT \cos(2\omega_i t)}{4Q\omega_i^2} \right) \right\rangle^{-1}. \quad (57) \]

To estimate the optimum Nosé mass for multiple oscillators we can modify (50) using (54)-(56) to obtain,

\[ \max(p_s) = \max \left( a \sum_{i=0}^{N} kT \sin(2\omega_i t) \right), \quad (58) \]

where \( a \leq 2 \) from (43). Solutions for \( p_s^* \), \( p_s \) on the auxiliary variable phase-space bounding curve (5), when \( s \) is at an average value (14), are,

\[ p_s^* = \sqrt{2QNkT} \], \quad (59)

and will be the point where \( p_s \) is at its maximum. The optimum value for \( Q \) will occur when (58) and (59) are equal.

If we consider a system where all of the oscillators are of similar frequency, \( \omega \), and set \( a = 2 \), the upper bound for \( a \), we have,

\[ \max(p_s) \leq \frac{NkT}{\omega}, \quad (60) \]
giving optimum $Q$,

$$Q \leq \frac{NkT}{2\omega^2}.$$  \hspace{1cm} (61)

Compare this with Nosé’s estimate $Q = \frac{2NkT}{\omega^2}$. As before a more accurate estimate for $a$ could be obtained, but this would only be useful for very specific cases as it is unlikely that all of the oscillators will be of exactly the same frequency. For mixed frequency systems the model (55)-(56) can be used to accurately predict the optimum value of $Q$, which was not previously possible using linearization methods.

However, if we compare the auxiliary variable phase space for 4 harmonic oscillators of different frequencies with that of the single harmonic oscillator, we see that the area of phase space used is similar in both examples, see Figure 8. This is expected as the probability of the entire system’s energy residing in the auxiliary variables is small. It addition is shown in Section 4 (78) that if the auxiliary variables were homogeneously distributed then we would have $\langle p_s^2/Q \rangle = NkT$ which is contrary to both the results in Section 2.2 and the values predicted by the equipartition theorem.

If we assume that there is no correlation between the dynamics of each body, the trajectories are random in relation to each other, then we can analyze this as follows. The auxiliary variable momentum, $p_s$, is driven by the variations in the kinetic energy of the system, as we can see from it’s equations of motion. As the dimension, $N$, of the system increases the variations in kinetic energy will now be reduced by a factor $1/\sqrt{N}$ and hence the magnitude of $p_s$ will increase by $\sqrt{N}$ rather than by $N$ as assumed in (60). If we substitute $\sqrt{N} \tilde{p}_s = p_s$ into
(5), where $E = \tilde{H}_0$ we get,

$$s = \exp \left( \frac{\tilde{H}_0}{NkT} - \frac{\tilde{p}_s^2}{2QkT} \right),$$

(62)

which coincides with both the auxiliary variable phase-space for the single harmonic oscillator, and the results obtained experimentally as shown in Figure 8.

For the calculation of the Nosé mass we now have, for oscillators of similar frequency close to $\omega$,

$$\max (\tilde{p}_s) = \frac{\sqrt{NkT}}{\omega},$$

(63)

and a bound on $\tilde{p}_s$ at $\langle s \rangle$ of,

$$\tilde{p}_s = \sqrt{2QkT},$$

(64)

giving optimum $Q = NkT/(2\omega^2)$, the same as in (61). Experiments with 4-8 oscillators indicate that using the masses predicted by Nosé’s linearization method do not give sampling in the canonical ensemble, the onset of this behavior occurring close to the prediction of (61).

3 Multiple Thermostat Methods.

In this section we develop the new Recursive Multiple Thermostatting scheme and show that it samples from the canonical ensemble. We will actually show this for a more general formulation of momentum scaling methods from which the RMT method is derived.

Given a Hamiltonian system where $H(q, p)$ is the energy of an $N$-body system, $q = (q_1, q_2, \cdots, q_N)$ and $p = (p_1, p_2, \cdots, p_N)$ are the positions and momenta of the $N$ bodies, a generalized Hamiltonian formulation for this class of thermostat is given by,

$$H_{GT}(q, p, s_1, s_2, \cdots, p_{s_1}, p_{s_2}, \cdots) = H\left(q, \frac{p}{s_1, s_{i_2}, \cdots}\right) + H_G(s_1, s_2, \cdots, p_{s_1}, p_{s_2}, \cdots),$$

(65)

where $s_1, s_2, \cdots$ are the auxiliary variables, $p_{s_1}, p_{s_2}, \cdots$ the auxiliary variables momenta, $\{s_{i_1}, s_{i_2}, \cdots\}$ is the set of auxiliary variables which scale the momenta of the original system, and $H_G$ the part of the revised Hamiltonian which dictates the dynamics of the auxiliary variables. Since rescaling the momentum also rescales time it is appropriate to apply a time reparametrization in the revised system using either a Sundman (as in the Nosé-Hoover formulation [4]) or Poincaré transformation as in [3]. When there is no time rescaling, or when it is
done using a Poincaré transformation, the resulting system has a Hamiltonian structure, and it is possible to show analytically that the modified system samples from the canonical ensemble subject to certain constraints. It is primarily these methods that will be considered here.

### 3.1 Multiple Thermostats.

It is possible to introduce additional thermostats into the Nosé and Nosé-Poincaré methods while retaining both their Hamiltonian structure and sampling from the canonical ensemble. This can be illustrated in a more general setting by rewriting the Nosé method, (1), to include the momenta of the thermostating variable with the system momenta such that \( \hat{p} = (p_1, p_2, \ldots, p_N, p_{N+1}) \) to give,

\[
H_N(q, s_1, \hat{\hat{p}}) = \hat{H}_N \left( q, \frac{p_1}{s_1}, \frac{p_2}{s_1}, \ldots, \frac{p_N}{s_1}, \frac{p_{N+1}}{s_1} \right) + (N + 1)kT \ln s_1
\]

where,

\[
\hat{H}_N(q, \hat{\hat{p}}) = H(q, p_1, p_2, \ldots, p_N) + \frac{p_{N+1}^2}{2Q_1},
\]

and,

\[
\hat{\hat{p}} = (p_1, p_2, \ldots, p_N, p_{N+1}) = \left( \frac{p_1}{s_1}, \frac{p_2}{s_1}, \ldots, \frac{p_N}{s_1}, \frac{p_{N+1}}{s_1} \right).
\]

A second thermostat can be added as follows,

\[
H_{NT}(q, s_1, s_2, \hat{\hat{p}}, p_{N+2}) = \hat{H}_N \left( q, \frac{p_1'}{s_2}, \ldots, \frac{p'_N}{s_2}, \frac{p'_{N+1}}{s_2} \right)
\]

\[
+ (N + 1)kT \ln s_1 + \frac{p_{N+2}^2}{2Q_2} + gkT \ln s_2 + f_2(s_2),
\]

where \( f_2(s_2) \) is a real valued function, \( g \) is a scalar and the new thermostat is applied to \( M \) of the momenta, the thermostatted set being \( \{p'_{i_1}, \ldots, p'_{i_M}\} \) and the non-thermostatted set being \( \{p'_{j_1}, \ldots, p'_{j_{N+1-M}}\} \) for some integers \( i_1, \ldots, i_M, j_1, \ldots, j_{N+1-M} \). Note that the thermostatted set may include any of the system momenta and the thermostating variable momenta. The partition function for this method, for energy \( E \), is defined as,

\[
Z = \frac{1}{N!} \int dp_{N+2} \int ds_2 \int ds_1 \int d\hat{\hat{p}} \int dq \delta [H_{NT} - E].
\]

We can substitute \( p'_{i} = p_i/s_1 \quad 1 \leq i \leq N, \quad p'_{N+1} = p_{N+1} \), the volume element then becomes \( d\hat{\hat{p}} = s_1^N d\hat{\hat{p}}' \), where \( \hat{\hat{p}}' \) is defined as above. There is no upper limit
in momentum space so we can change the order of integration of \(d\hat{p}'\) and \(ds_1\) giving,

\[
Z = \frac{1}{N!} \int dp_{N+2} \int ds_2 \int d\hat{p}' \int dq \int ds_1 s_1^N \delta [H_{NT} - E].
\]

Using the equivalence relation for \(\delta\), \(\delta[g(x)] = \delta[x - x_0]/|g'(x)|\), where \(x_0\) is the zero of \(g(x) = 0\), for \(x = s_1\), and noting that \(s_1 > 0\) is assumed as a natural consequence of the form of the Hamiltonian, we get,

\[
Z = \frac{1}{N!(N+1)kT} \int dp_{N+2} \int ds_2 \int d\hat{p}' \int dq \exp \left( -\left( \hat{H}_N + \frac{p_{N+2}^2}{2s_2^2} + gkT \ln s_2 + f_2(s_2) - E \right) \right).
\]

We can substitute \(p'_{N+1} = p'_l/s_2\) \(l \in \{i_1, \cdots, i_M\}\), \(p''_l = p''_l\) \(l \in \{j_1, \cdots, j_{N+1-M}\}\) the volume element then becomes \(d\hat{p}' = s_2^M d\hat{p}''\) where \(\hat{p}'' = (p''_1, p''_2, \cdots, p''_{N+1})\). There is no upper limit in momentum space so we can change the order of integration of \(d\hat{p}''\) and \(ds_2\) giving,

\[
Z = \frac{1}{N!(N+1)kT} \int dp_{N+2} \int d\hat{p}'' \int dq \int ds_2 \int s_2^M \exp \left( -\left( \hat{H}_N(q, \hat{p}'') + \frac{\hat{p}'_{N+2}^2}{2s_2^2} + gkT \ln s_2 + f_2(s_2) - E \right) \right).
\]

If we chose \(g = M\) and suppose that,

\[
\int_0^\infty \exp \left( -\frac{f_2(x)}{kT} \right) \, dx = K_2 < \infty,
\]

then,

\[
Z = \frac{K_2}{N!(N+1)kT} \int dp_{N+2} \int d\hat{p}'' \int dq \exp \left( -\left( \hat{H}_N(q, \hat{p}'') + \frac{\hat{p}'_{N+2}^2}{2s_2^2} - E \right) \right).
\]

Integrating over both thermostat momenta, \(\hat{p}''_{N+1}\) and \(p_{N+2}\), gives,

\[
Z = \frac{C}{N!} \int d\hat{p}'' \int dq \exp \left( -\frac{H(q, \hat{p}'')}{kT} \right),
\]
where,
\[ C = \frac{2\pi K_2 \sqrt{Q_1 Q_2}}{N + 1} \exp \left( \frac{E}{kT} \right), \]
and,
\[ p'' = (p''_1, p''_2, \cdots, p''_N). \]

This process can be repeated to add more thermostats, with the possibility at each stage of thermostatting the previous thermostat’s momentum in addition to any of the other momenta. A similar proof can be applied to the Nosé-Poincaré method.

3.2 Multiple Thermostat Schemes.

The general Hamiltonian for this class of methods, with \( M \) thermostats, will then be,
\[ H_{NM} = \sum_{j=1}^{N} \frac{p_j^2}{2m_j s_{k_1}^2 \cdots s_{k_m}^2} + V(q) + \sum_{i=1}^{M-1} \frac{p_{s_{i+1}}^2}{2Q_i \psi_i} + \frac{p_{s_{M}}^2}{2Q_M} \\
+ g kT \ln s_1 + \sum_{i=2}^{M} (g_i kT \ln s_i + f_i(s_i)) \]  
(68)

where \( g = N + 1 \). The original system is thermostatted by a subset of the thermostats, \( \{s_{k_1}, s_{k_2}, \cdots, s_{k_m}\} \), with \( \{k_1, k_2, \cdots, k_m\} \subseteq \{1, 2, \cdots, M\} \). The \( i \)th thermostat is thermostatted by \( \psi_i \) defined as,
\[ \psi_i = \prod_{j=1}^{n_i} s_{l_j}^2, \]
where \( \{l_1, l_2, \cdots, l_{n_i}\} \subseteq \{i+1, i+2, \cdots, M\} \). \( g_i \) is the number of degrees of freedom thermostatted by the \( i \)th thermostat and the auxiliary functions, \( \{f_i(s_i)\} \), are real valued satisfying,
\[ \int_0^\infty \exp \left( \frac{-f_i(x)}{kT} \right) \, dx = K_i < \infty. \]  
(69)

Remark: The Nosé-Poincaré variation can be produced by applying a Poincaré time transformation to (68) using a time reparametrization variable equal to \( s_{k_1} s_{k_2} \cdots s_{k_m} \), and setting \( g = N \).

3.3 Nosé-Poincaré chains.
Nosé-Poincaré chains can be derived from (68) as follows,

\[
H_{NPC} = s_1 \left[ H \left( q, \frac{p}{s_1} \right) + \sum_{i=1}^{M-1} \frac{p_{s_i}^2}{2Q_i s_{i+1}^2} + \frac{p_{s_M}^2}{2Q_M} + NkT \ln s_1 \\
+ \sum_{i=1}^{M} (kT \ln s_i + f_i(s_i)) - H_0 \right]
\]  

(70)

where the auxiliary functions \( \{f_i(s_i)\} \) are real valued and satisfy equation (69) and \( H_0 \) is chosen such that \( H_{NPC} = 0 \) when evaluated at the initial conditions.

As discussed in Section 1, the stability of the numerical implementation of chains is not as good as the underlying Nosé-Poincaré method and the low dimension of the sub-system to be thermostatted by each new thermostat means that the expected average value of \( p^2 s_i / (Q_i s_{i+1}^2) \) may not be easily achievable, as demonstrated by the results in Table 3. To overcome these deficiencies while retaining the insensitivity to the values of the Nosé masses requires a new approach to the problem.

### 3.4 Recursive Nosé/Nosé-Poincaré Thermostats.

An alternative approach is to apply a Nosé thermostat to the original Hamiltonian, then apply a second thermostat to all of the “kinetic” terms in the new Hamiltonian, including the term for \( p_{s_1} \), the thermostating variable momentum. This method can then be applied recursively to add as many thermostats as required with the dimension of the system to be thermostatted increasing for each thermostat. This leads to better stability when compared with chains, as the time reparametrization involves all of the thermostats, and generally requires only one additional thermostat even for low dimensional systems. The Hamiltonian for the formulation without time rescaling, with \( M \) thermostats will be,

\[
H_{NR} = \sum_{j=1}^{N} \frac{p_j^2}{2m_j s_1^2 s_2^2 \cdots s_M^2} + V(q) + \sum_{i=1}^{M-1} \frac{p_{s_i}^2}{2Q_i s_{i+1}^2 s_M^2} + \frac{p_{s_M}^2}{2Q_M} \\
+ gkT \ln s_1 + \sum_{i=2}^{M} ((N + i - 1)kT \ln s_i + f_i(s_i))
\]  

(71)

where \( g = N + 1 \) and the auxiliary functions, \( \{f_i(s_i)\} \), are real valued satisfying equation (69).

The Nosé-Poincaré method is derived from this by applying a rescaling of time by \( s_1 s_2 \cdots s_M \),

\[
H_{NP} = s_1 s_2 \cdots s_M \left[ H_{NR} - H_0 \right],
\]  

(72)

where \( H_0 \) is chosen such that \( H_{NP} = 0 \) at initial conditions and setting \( g = N \).
3.5 Choice of the Auxiliary Function.

For the additional thermostats to work correctly an auxiliary function, \( f_i(s_i) \), must be chosen not only to satisfy equation (69) but to provide a suitable modification to the thermostats. One such choice is,

\[
f_i(s_i) = \frac{(a_i - s_i)^2}{2C_i},
\]

where \( C_i \), the auxiliary function coefficient, is a constant. The value \( a_i \) is chosen as the required average value of \( s_i \), generally 1, as the additional term will operate as a negative feedback loop to minimize \((a_i - s_i)\), as can be seen from the equations of motion. For a Hamiltonian as given in (2), the equations of motion for \( p_{s_i} \) and \( s_i \) in the equivalent Nosé chain system will be,

\[
\dot{p}_{s_i} = p_{s_i} - \frac{kT}{s_i} + \frac{(a_i - s_i)}{C_i}, \quad \dot{s_i} = \frac{p_{s_i}}{Q_i s_i^{3} + 1}.
\]

(74)

Assuming \( C_i \) is sufficiently small, if \( s_i \) increases above \( a_i \) then \( p_{s_i} \) will decrease, eventually decreasing \( s_i \). Conversely, if \( s_i \) decreases below \( a_i \) then \( p_{s_i} \) will increase, eventually increasing \( s_i \).

In the context of Nosé-Poincaré chains the value of \( C_i \), \( i \geq 2 \) can be estimated by considering the equations of motion for the \( i^{th} \) thermostat (74). From this we see that \( s_i \) is driven by the changes in \( p_{s_{i-1}} \). The purpose of the auxiliary function is to limit the excursions of \( s_i \), which can be achieved if \( ds_i / dp_{s_{i-1}} \) is a maximum at \( s_i = a_i \). From this it was shown in [2] that \( C_i \) should satisfy,

\[
C_i \leq \frac{a_i^2}{8kT}.
\]

(75)

4 Analysis of Multiple Thermostat schemes.

With the introduction of multiple thermostats it is now possible to have multiple Nosé masses. From the analysis in Section 2, we can see that a good choice of masses occurs where the auxiliary variables approach their phase-space boundary, and expected averages. From this we conclude that the introduction of multiple thermostats can be used to enforce the ergodicity of the system.

4.1 Expected average values for \( p_s^2/Q \).

If we consider the single harmonic oscillator thermostatted by the Nosé-Poincaré method, from (36) and (37) we would expect that the maximum value of \( p_s \) to occur when \( s \) is at its average value, where the phase-space boundary for \( p_s \) is given by (35) as \( \sqrt{2QkT} \). This, together with the observation from (36)
that \( \max(p_s^2) = 2 \langle p_s^2 \rangle \), gives,

\[
\langle \frac{p_s^2}{Q} \rangle = kT.
\] (76)

From this we observe that the average value of \( p_s^2/Q \), when \( Q \) is greater than the “optimum” value, is always less than \( kT \), which is observed in practice and illustrated in Figure 3.

If the phase-space trajectories of the auxiliary variables were homogenously distributed we could calculate the average value from the auxiliary variable phase-space using (5). Here the probability density function for \( p_s \) would be,

\[
\rho_{p_s} = \frac{\exp\left(-\frac{p_s^2}{2QkT}\right)}{\int_{-\infty}^{\infty} \exp\left(-\frac{p_s^2}{2QkT}\right) dp_s},
\] (77)

then,

\[
\langle \frac{p_s^2}{Q} \rangle = \int_{-\infty}^{\infty} \frac{p_s^2}{Q} \rho_{p_s} dp_s = NkT.
\] (78)

For the single harmonic oscillator, where \( N = 1 \), this would give the same result as (15), but would raise some interesting questions for multiple oscillators.

4.2 Obtaining expected average values independently of \( Q \).

From Figure 3 it is clear that the correct choice of \( Q \) is limited to a very narrow band but from the discussion above another possibility presents itself, that of thermostatting the thermostat to ensure that \( \langle p_s^2/Q \rangle = kT \). A variation of this, Nosé-Hoover chains, was first proposed by Martyna, Klein and Tuckerman in [8] and was seen as providing additional ergodicity to the system so that the modified system sampled from the canonical ensemble. In [8] it was shown that the single harmonic oscillator could be successfully thermostatted by this method. In Figure 9, \( \langle p_s^2/Q \rangle \) is plotted against \( Q \) for a Nosé-Poincaré chains integrator consisting of 5 thermostats with \( Q_j = 2Q \) and \( C_j = 0.08 \) where \( kT = 1 \). From this we see that the range of \( Q \) is increased and that chains can also limit the activity of the auxiliary variables, preventing them from entering self-oscillation.

As discussed in Section 3.3, the required average value of \( p_{s_i}^2/(Q_i s_{i+1}^2) \) for each thermostat may not be achievable. If we consider the Nosé-Poincaré chains Hamiltonian (70) the average values for \( p_{s_i}^2/(Q_i s_{i+1}^2) \) can be obtained, if the system is ergodic, by substituting \( p_{s_i}^2/(Q_i s_{i+1}^2) \) for \( s \) in (7). In a method similar to that used in Section 2.2 we can substitute \( \tilde{p}_{s_i} = p_{s_i}/s_{i+1} \) and use the equivalence relation for \( \delta \) in both the denominator and numerator of the new equation.
Noting that,
\[
\int_{-\infty}^{\infty} s_j \exp\left(-\frac{(a_j - s_j)^2}{C_j}\right) ds_j = \int_{-\infty}^{\infty} \exp\left(-\frac{(a_j - s_j)^2}{C_j}\right) ds_j,
\]
and that,
\[
\int_{-\infty}^{\infty} \frac{\tilde{p}_{s_i}^2}{Q_i} \exp\left(-\frac{\tilde{p}_{s_i}^2}{2Q_i kT}\right) dp_{s_i} = kT \int_{-\infty}^{\infty} \exp\left(-\frac{\tilde{p}_{s_i}^2}{2Q_i kT}\right) dp_{s_i},
\]
the new equation reduces to,
\[
\langle \frac{\tilde{p}_{s_i}^2}{Q_i s_i^2} \rangle = kT.
\]
Similarly we can show,
\[
\langle \frac{\tilde{p}_{s_M}^2}{Q_M s_M^2} \rangle = kT.
\]

For a Nosé-Poincaré chains integrator consisting of 5 thermostats with $Q_i = 2Q$ and $C_j = 0.08$ where $kT = 1$, integrated over 20,000,000 steps of 0.01 gave the averages in Table 3. Even if the dimension of the underlying system is increased this problem persists, hence the system is not ergodic and the proof of sampling from the canonical ensemble is invalid.

An alternative solution is to use Recursive Thermostatting (71) and (72), introduced in Section 3.4, where the complete system, including the preceding thermostat, is thermostatted. This means that each new thermostat will thermostat a system of increasing dimension, and where the underlying system is
large, sampling will be close to the canonical ensemble. It has been found that, even for low dimensional systems, one additional thermostat is usually sufficient to provide good sampling. As discussed in Section 3.3, stability is also increased when compared to chains, allowing larger step sizes. In Figure 9 we see that the range of possible values for \( Q \) is vastly increased, and the average value of \( \frac{p_{s_i}^2}{Q_i s_{i+1}^2} \) is closer to 1, when compared to the Nosé-Poincaré chains method, as seen in Table 3.

### 4.3 Obtaining expected average values Independently of \( Q \) for Multiple Oscillators.

In Section 4 we saw that \( \langle \frac{p_{s_i}^2}{Q} \rangle = kT \), based on the model in Section 2.3, was sufficient for the auxiliary variables to interact with their phase-space boundary for a single harmonic oscillator, giving rise to the behavior required to sample from the canonical ensemble. In Section 2.7 it was shown that the volume of auxiliary variable phase-space sampled by the system is essentially independent of the number of oscillators being considered, despite the increase in the available volume from (5), if the system is ergodic. From this we would expect that thermostating the thermostat to ensure that \( \langle \frac{p_{s_i}^2}{Q} \rangle = kT \) would give good results for multiple oscillators, with a much reduced dependence on \( Q \), as we saw for the case of the single harmonic oscillator, and this can be seen in experiments. However there may be additional benefits for multiple oscillators and these can be classified for systems consisting of oscillators of similar frequency and multi-scale systems.

#### 4.3.1 Multiple Oscillators of similar frequency.

The boundary derived in Section 2.7 assumes random interaction between the oscillators and is easily seen where the oscillators are synchronous, or where there is some correlation between the oscillators and the system is of small dimension, different results can be produced as shown in Figure 10, left hand

<table>
<thead>
<tr>
<th>i</th>
<th>Chains ( \langle \frac{p_{s_i}^2}{Q_i s_{i+1}^2} \rangle )</th>
<th>Recursive ( \langle \frac{p_{s_i}^2}{Q_i s_{i+1}^2} \rangle )</th>
<th>Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.987</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>2</td>
<td>0.678</td>
<td>0.973</td>
<td>1.000</td>
</tr>
<tr>
<td>3</td>
<td>0.543</td>
<td>N/A</td>
<td>1.000</td>
</tr>
<tr>
<td>4</td>
<td>0.484</td>
<td>N/A</td>
<td>1.000</td>
</tr>
<tr>
<td>5</td>
<td>0.525</td>
<td>N/A</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Table 3: Average values for \( \frac{p_{s_i}^2}{Q_i s_{i+1}^2} \) using Chains and Recursive methods.
side graph. In this example there are 4 oscillators with $\omega_1 = 1.012$, $\omega_2 = 0.992$, $\omega_3 = 1.021$, $\omega_4 = 1.000$, Nosé mass 1.2 and we find that $\langle p_s^2 / Q \rangle = 3.144$. Compare this result with the correct value $\langle p_s^2 / Q \rangle = 1$ and the value predicted from (78) of $\langle p_s^2 / Q \rangle = 4$. Clearly, in this case, thermostatting $p_s$ should have a dramatic effect on the results, as seen in the right hand side graph of Figure 10, where $\langle p_s^2 / Q \rangle = 1.010$ leading to much faster convergence to the canonical ensemble.

4.3.2 Multiple Oscillators in Multi-Scale Systems.

In systems where there is no correlation between the oscillators, for example in a multi-scale system, we would expect the only interaction to be between the oscillators and the auxiliary variables. When sampling from the canonical ensemble the $l^{th}$ oscillator would be expected to pass through the point $\tilde{p}_l = 0$, $q_l = 0$ at which point all of the energy for that oscillator must reside in the auxiliary variables, based on the assumption above. By separating $s$ into dynamic and average values such that $s = \tilde{s}(s)$, the auxiliary variable phase-space bound (62) can be re-written, using (14), as,

$$\frac{\dot{\tilde{p}}^2}{2Q} + kT \ln \tilde{s} = \frac{\tilde{H}_0}{N} - kT \ln \langle s \rangle = kT.$$  \hspace{1cm} (83)
Figure 11: Kinetic energy for 3 oscillators using RMT and Nosé-Poincaré methods for $kT = 1$. 

From the above argument this is also an upper bound for the $l^{th}$ oscillator energy and hence,

$$\frac{p_l^2}{2m_l} + \frac{q_l^2}{2} \leq kT.$$  \hspace{1cm} (84)

Taking averages, and noting that the sum of the energies of all oscillators is $NkT$, yields,

$$\left\langle \frac{p_l^2}{2m_l} + \frac{q_l^2}{2} \right\rangle = kT.$$ \hspace{1cm} (85)

From this we anticipate that by thermostatting the thermostat, such that $\left\langle \frac{\tilde{p}_s^2}{Q} \right\rangle = kT$ and the auxiliary variable phase space is bounded by (62), the equipartition of energy between the oscillators would be enforced. Using the RMT method in comparison to the standard Nosé-Poincaré method we see that indeed this is the case as shown in Figure 11, where 3 oscillators with frequencies $\omega_1 = 1.000$, $\omega_2 = 0.308$, $\omega_3 = 0.095$, Nosé mass 8 and a step size 0.05 are simulated. The kinetic energies are calculated for each oscillator using running averages of 1,000,000 steps. Since the equipartition of energy can be shown for systems of harmonic oscillators which sample from the canonical ensemble, convergence to the canonical ensemble is considerably faster.

\hspace{1cm} 2Remark: Fast Thermostatting can be accomplished use of the RMT scheme. In traditional thermostatting schemes the optimum value for $Q$, from (61), increases with the dimension of the system resulting in a dramatic increase in thermostat response time for large systems, which may be undesirable. From Figure 9 we see that thermostatting the thermostat gives a vastly increased range for $Q$ which allows very small values to be used, giving a much faster response.

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5 Conclusion.

It is often assumed that Nosé’s method works by using the Nosé mass to tune the self-oscillation frequency of the auxiliary variables to resonate with some natural frequency within the system to be simulated. In fact, no matter what the value of $Q$, the auxiliary variables oscillate at the first harmonics of any frequencies within the system, introducing a potential 2:1 resonance, as shown on the model in Section 2.3. These first harmonics persist as the system moves into the canonical ensemble (with additional oscillations at the fundamental frequencies, as seen in Figure 12, for an oscillator with frequency 0.167Hz showing the fourier analysis of $p_s$) when interactions with the auxiliary variable phase-space boundary occur and coincide with more chaotic behavior of the system. It is clear that to sample from the canonical ensemble the phase-space variables must approach their boundary and this can be induced by the correct choice of $Q$, or by controlling the thermostat so that it’s canonical ensemble average is achieved. In the latter case the Recursive Thermostatting technique has proven to overcome many of the difficulties of previous methods, and generally requires fewer thermostats.

Recursive Thermostatting has benefits in situations where the system consists of oscillators of similar frequencies, where Nosé dynamics leads to a large part of the auxiliary variable phase space being sampled, and hence too great a value for $\langle p_s^2/Q \rangle$ giving incorrect sampling, and in multi-scale systems, where the equipartition of energy, and hence isothermal behavior, is difficult to achieve. In addition the large range of choice for the Nosé mass allows for the use of small masses, and hence fast thermostatting, which is useful for large systems where traditionally a large Nosé mass is required.
6 Acknowledgments

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References


Appendices

A Hamiltonian Splitting Method for RMTs.

The numerical methods used for the following experiments are based on the following general Hamiltonian,

\[ H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(q), \]

where \( q = (q_1, \ldots, q_N) \). The RMT method derived from this, with \( M \) thermostats based on the auxiliary function in equation (73) is then,

\[
H_{NR} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(q) + \sum_{j=1}^{M-1} \frac{p_{s_j}^2}{2Q_j s_{j+1}^2 \cdots s_M^2} + \frac{p_{s_M}^2}{2Q_M} + gkT \ln s_1
\]

\[
+ \sum_{j=2}^{M} \left( (N + j - 1)kT \ln s_j + \frac{(a_j - s_j)^2}{2C_j} \right),
\]

where \( g = N + 1 \), giving a Nosé-Poincaré multiple thermostat method, with \( g = N \),

\[
H_{NPR} = s_1 s_2 \cdots s_M [H_{NR} - H_0],
\]

where \( H_0 \) is chosen as the initial value of \( H_{NR} \). The equations of motion are,

\[
\dot{q}_i = \frac{p_i}{m_i s_1 \cdots s_M},
\]

\[
\dot{p}_i = -s_1 \cdots s_M \frac{\partial V(q)}{\partial q_i},
\]

\[
\dot{s}_1 = \frac{s_1 \cdots s_M \hat{p}_{s_1}}{Q_1 s_2^2 \cdots s_M^2},
\]

\[
\dot{p}_{s_1} = s_2 \cdots s_M \left( \sum_{i=1}^{N} \frac{p_i^2}{m_i s_1^2 \cdots s_M^2} - NkT - H_{NR}(q, p, s, \hat{p}_s) + H_0 \right),
\]

\[
\dot{s}_j = \frac{s_1 \cdots s_M \hat{p}_{s_j}}{Q_j s_{j+1}^2 \cdots s_M^2},
\]

\[
\dot{p}_{s_j} = s_1 \cdots s_M \left( \sum_{i=1}^{N} \frac{p_i^2}{m_i s_1^2 \cdots s_M^2} + \sum_{l=1}^{j-1} \frac{p_{s_l}^2}{Q_l s_{l+1}^2 \cdots s_M^2} \right)
\]

\[
- \frac{(N + j - 1)kT}{s_j} + \frac{a_j - s_j}{C_j} \frac{H_{NR}(q, p, s, \hat{p}_s) - H_0}{s_j}, \quad 1 < j < M,
\]

\[
\dot{s}_M = \frac{s_1 \cdots s_M \hat{p}_{s_M}}{Q_M},
\]
\[
\dot{p}_s = s_1 \cdots s_M \left( \sum_{i=1}^{N} \frac{p_i^2}{m_i s_1^2 \cdots s_{M-1}^2 s_M^2} + \sum_{l=1}^{M-1} \frac{p_{s_l}^2}{Q_l s_{l+1}^2 \cdots s_{M-1}^2 s_M^2} - \frac{(N + M - 1)kT}{s_M} + \frac{a_M - s_M}{C_M} - \frac{H_{NR}(q, p, s, \hat{p}_s) - H_0}{s_M} \right),
\]
where \( s = (s_1, \ldots, s_M) \), \( \dot{p}_s = (p_{s_1}, \ldots, p_{s_M}) \) and \( p = (p_1, \ldots, p_N) \). The thermostats have introduced an implicit coupling into the equations of motion, but an explicit method can be formulated by splitting the Hamiltonian and corresponding Liouville operator. For \( M \) thermostats this can be done using \( 2 + M \) Hamiltonians by employing a separate Hamiltonian for each extended variable “kinetic” term. Then if,
\[
H = H_1 + H_2 + H_{3_1} + \cdots + H_{3_M},
\]
we have,
\[
H_1 = s_1 \cdots s_M \left[ \sum_{i=1}^{N} \frac{p_i^2}{2m_i s_1^2 \cdots s_{M-1}^2 s_M^2} + NkT \ln s_1 \right],
\]
\[
H_2 = s_1 \cdots s_M \left[ V(q) + \sum_{j=2}^{M} \left( (N + j - 1)kT \ln s_j + \frac{(a_j - s_j)^2}{2C_j} \right) \right],
\]
\[
H_{3_1} = s_1 \cdots s_M \left[ \frac{p_{s_1}^2}{2Q_1 s_2^2 \cdots s_M^2} - H_0 \right],
\]
\[
H_{3_j} = s_1 \cdots s_M \left[ \frac{p_{s_j}^2}{2Q_j s_{j+1}^2 \cdots s_M^2} \right], \quad 1 < j < M,
\]
\[
H_{3_M} = s_1 \cdots s_M \left[ \frac{p_{s_M}^2}{2Q_M} \right].
\]
Using a symmetric splitting of the Liouville operator to get a symplectic and time reversible method,
\[
iL_H = \{, H\} = \{, H_1\} + \{, H_2\} + \{, H_{3_1}\} + \cdots + \{, H_{3_M}\} = iL_{H_1} + iL_{H_2} + iL_{H_{3_1}} + \cdots + iL_{H_{3_M}}.
\]
This splitting introduces an error of order \( \Delta t^3 \) at each step in terms of the solution operator, giving a second order method,
\[
\Psi_H(\Delta t) = e^{iL_{H_1} \Delta t},
\]
\[
= e^{iL_{H_2} \Delta t/2} e^{iL_{H_{3_1}} \Delta t/2} \cdots e^{iL_{H_{3_M}} \Delta t/2} e^{iL_{H_{3_M}} \Delta t/2} e^{iL_{H_{3_M}} \Delta t/3} + O(\Delta t^3).
\]
The dynamics for \( H_1 \) and \( H_2 \) can be solved in a straightforward manner, leaving \( H_{3_1} \cdots H_{3_M} \) to be solved either analytically or by using the generalized leapfrog algorithm as described in [3].