

The Canonical Ensemble via Symplectic Integrators using Nosé and Nosé-Poincaré chains.

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(Dated: March 26, 2004)

Abstract

Simulations that sample from the canonical ensemble can be generated by the addition of a single degree of freedom, provided that the system is ergodic, as described by Nosé with subsequent modifications by Hoover to allow sampling in real time. Nosé-Hoover dynamics is not ergodic for small or stiff systems and the addition of auxiliary thermostats is needed to overcome this deficiency. Nosé-Hoover dynamics, like its derivatives, does not have a Hamiltonian structure, precluding the use of symplectic integrators which are noted for their long term stability and structure preservation. As an alternative to Nosé-Hoover, the Hamiltonian Nosé-Poincaré method was proposed by Bond, Laird and Leimkuhler [S.D. Bond, B.B. Laird and B.J. Leimkuhler, *J. Comp. Phys.*, **151**, 114, (1999)], but the straightforward addition of thermostating chains does not sample from the canonical ensemble. In this paper a method is proposed whereby additional thermostats can be applied to a Hamiltonian system while retaining sampling from the canonical ensemble. This technique has been used to construct thermostating chains for the Nosé and Nosé-Poincaré methods.

I. INTRODUCTION

a. Nose dynamics and its derivatives¹⁻⁷ are popular schemes for implementing molecular simulations at constant temperature. In all such schemes, sampling from the canonical ensemble is conditional on the system being ergodic, and in small or stiff systems this is often not the case. To overcome the lack of ergodicity in these systems further modifications to the Nosé-Hoover method were proposed by Martyna, Klein and Tuckerman⁸ with new thermostats added to control each previous thermostat to form a thermostating chain. This method is successful but suffers from the limitations of the Nosé-Hoover method: there is no Hamiltonian from which it is derived and hence symplectic methods are not applicable. More recently the real time Nosé-Poincaré method was proposed by Bond, Laird and Leimkuhler⁶ which is based on an extended Hamiltonian, but the application of thermostating chains to the Nosé-Poincaré method in a straightforward manner does not result in sampling from the canonical ensemble. A generalized thermostating technique has been developed by Leimkuhler and Laird⁹; in this scheme an auxiliary heat bath is coupled into the thermostating variables, an example of the auxiliary heat bath is a box containing billiards. This requires the design of the auxiliary heat bath and can require long integration time for the correct sampling to occur if the bath is poorly chosen.

This paper introduces the idea of adding multiple thermostats to a Hamiltonian which has been modified by Nosé's method, while retaining sampling from the canonical ensemble. Here we employ a regularizing term in the Nosé or Nosé-Poincaré Hamiltonian to ensure bounded integrals over the auxiliary variables. This technique is used to introduce additional terms into the thermostating chain in both the Nosé and Nosé-Poincaré Hamiltonians, it is then possible to prove analytically that they sample from the canonical ensemble. In addition the fast convergence to the canonical ensemble, which is a characteristic of the Nosé-Hoover chains, is observed. Before proceeding to describe the new thermostating technique, we introduce the Nosé-Poincaré formulation and other elements on which our method is based.

A. Nosé and Nosé-Hoover schemes.

b. Nosé's method¹ adds a thermostating variable to the equations of motion to act as a heat bath. Given a Hamiltonian system where $H(q, p)$ is the energy of an N -body

system, $q = (q_1, q_2, \dots, q_N)$ and $p = (p_1, p_2, \dots, p_N)$ are the positions and momenta of the N bodies, Nosé proposed the extended Hamiltonian:

$$H^{Nosé}(q, s, p, p_s) = H\left(q, \frac{p}{s}\right) + \frac{p_s^2}{2Q} + (N+1)kT \ln s, \quad (1)$$

where s is the new thermostating variable, p_s its corresponding momentum, T is temperature, Q the Nosé mass and k is the Boltzmann constant. In the equations of motion for this Hamiltonian, the time is scaled by the thermostating variable s .

Hoover developed the idea of applying a Sundman transformation, $\frac{dt}{dt'} = s$, to correct the dynamics, but this destroys the Hamiltonian structure so that symplectic methods are no longer applicable. Applying the Sundman transformation, and substituting $p'_i = p_i/s$, $t' = \int dt/s$, $p'_s = p_s/s$, then making the substitution $p_\eta = Q(1/s)ds/dt'$, $\eta = \ln s$ the equations of motion become,

$$\frac{dq_i}{dt'} = \frac{p'_i}{m_i}, \quad (2)$$

$$\frac{dp'_i}{dt'} = -\nabla_{q_i} V(q) - p'_i \frac{p_\eta}{Q}, \quad (3)$$

$$\frac{d\eta}{dt'} = \frac{p_\eta}{Q}, \quad (4)$$

$$\frac{dp_\eta}{dt'} = \sum_{i=1}^N \frac{p_i'^2}{m_i} - NkT. \quad (5)$$

This form is now known as the Nosé-Hoover thermostat².

B. Nosé-Hoover chains.

c. Martyna, Klein and Tuckerman⁸ proposed a method to overcome the lack of ergodicity in small or stiff systems. Here each thermostat is controlled by another thermostat, forming a thermostat chain. In standard Nosé-Hoover dynamics the distribution has a Gaussian dependence on the particle momenta, p , as well as the thermostat momentum, p_η . The Gaussian fluctuations of p are driven by the thermostat but there is nothing to drive the fluctuations of p_η unless further thermostats are added as described above. The modified dynamics, for M thermostats, can then be expressed as,

$$\frac{dq_i}{dt'} = \frac{p'_i}{m_i}, \quad (6)$$

$$\frac{dp'_i}{dt'} = -\nabla_{q_i} V(q) - p'_i \frac{p_{\eta_1}}{Q_1}, \quad (7)$$

$$\frac{d\eta_i}{dt'} = \frac{p_{\eta_i}}{Q_i}, \quad (8)$$

$$\frac{dp_{\eta_1}}{dt'} = \left(\sum_{i=1}^N \frac{p_i^2}{m_i} - NkT \right) - p_{\eta_1} \frac{p_{\eta_2}}{Q_2}, \quad (9)$$

$$\frac{dp_{\eta_j}}{dt'} = \left(\frac{p_{\eta_{j-1}}^2}{Q_{j-1}} - kT \right) - p_{\eta_j} \frac{p_{\eta_{j+1}}}{Q_{j+1}}, \quad 1 < j < M, \quad (10)$$

$$\frac{dp_{\eta_M}}{dt'} = \left(\frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - kT \right). \quad (11)$$

These equations can be shown to produce the correct phase-space distributions.

C. Nosé-Poincaré method.

d. Neither the Nosé-Hoover or the Nosé-Hoover chain methods have a corresponding Hamiltonian which means that symplectic integrators, with their associated long term stability and structure preserving characteristics, are not applicable. The real time Nosé-Poincaré method was introduced (along with a symplectic integrator) by Bond, Laird and Leimkuhler⁶. The reformulation for a Hamiltonian system with energy $H(q, p)$ is,

$$H^{NP}(q, s, p, p_s) = \left(H \left(q, \frac{p}{s} \right) + \frac{p_s^2}{2Q} + NkT \ln s - H_0 \right) s. \quad (12)$$

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 the initial conditions.

The Nosé-Poincaré method has been extended to NPT ensemble simulation¹⁰ and shown there to be an efficient method. However, it can be shown that the application of thermostating chains to the Nosé-Poincaré method in a straightforward manner⁶ does not sample from the canonical ensemble.

II. MULTIPLE THERMOSTATS.

e. 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 $\hat{p} = (p_1, p_2, \dots, p_N, p_{N+1})$ to give,

$$\begin{aligned}
H^N(q, s_1, \hat{p}) &= \hat{H}^N\left(q, \frac{p_1}{s_1}, \frac{p_2}{s_1}, \dots, \frac{p_N}{s_1}, p_{N+1}\right) + (N+1)kT \ln s_1 \\
&= \hat{H}^N(q, \hat{p}') + (N+1)kT \ln s_1,
\end{aligned}$$

where,

$$\hat{H}^N(q, \hat{p}) = H(q, p_1, p_2, \dots, p_N) + \frac{p_{N+1}^2}{2Q_1},$$

and,

$$\begin{aligned}
\hat{p}' &= (p'_1, p'_2, \dots, p'_N, p'_{N+1}), \\
&= \left(\frac{p_1}{s_1}, \frac{p_2}{s_1}, \dots, \frac{p_N}{s_1}, p_{N+1}\right).
\end{aligned}$$

A second thermostat can be added as follows,

$$\begin{aligned}
H^{NT}(q, s_1, s_2, \hat{p}, p_{N+2}) &= \hat{H}^N\left(q, p'_{j_1}, \dots, p'_{j_{N+1-M}}, \frac{p_{i_1}'}{s_2}, \dots, \frac{p_{i_M}'}{s_2}\right) \\
&\quad + (N+1)kT \ln s_1 + \frac{p_{N+2}^2}{2Q_2} + gkT \ln s_2 + f_2(s_2),
\end{aligned}$$

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 $\{p'_{i_1}, \dots, p'_{i_M}\}$ and the non-thermostatted set being $\{p'_{j_1}, \dots, p'_{j_{N+1-M}}\}$ for some integers $i_1, \dots, i_M, j_1, \dots, j_{N+1-M}$. 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,

$$Z = \frac{1}{N!} \int dp_{N+2} \int ds_2 \int ds_1 \int d\hat{p} \int dq \delta(H^{NT} - E). \quad (13)$$

We can substitute $p'_i = p_i/s_1$ $1 \leq i \leq N$, $p'_{N+1} = p_{N+1}$, the volume element then becomes $d\hat{p} = s_1^N d\hat{p}'$, where \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 δ , $\delta(g(x)) = \delta(x - x_0)/|g'(x)|$, where x_0 is the zero of $g(x) = 0$, for $x = s_1$, and noting that $|s_1| = s_1$ since $\ln s_1$ is not defined for $s_1 < 0$, we get,

$$\begin{aligned}
Z &= \frac{1}{N!(N+1)kT} \int dp_{N+2} \int ds_2 \int d\hat{p}' \\
&\quad \int dq \exp\left(\frac{-\left(\hat{H}^N + \frac{p_{N+2}^2}{2Q_2} + gkT \ln s_2 + f_2(s_2) - E\right)}{kT}\right).
\end{aligned}$$

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

$$\begin{aligned} Z &= \frac{1}{N!(N+1)kT} \int dp_{N+2} \int d\hat{p}'' \int dq \\ &\quad \int ds_2 s_2^M \exp \left(\frac{-\left(\hat{H}^N(q, \hat{p}'') + \frac{p_{N+2}^2}{2Q_2} + gkT \ln s_2 + f_2(s_2) - E\right)}{kT} \right), \\ &= \frac{1}{N!(N+1)kT} \int dp_{N+2} \int d\hat{p}'' \int dq \int ds_2 s_2^{M-g} \exp \left(\frac{-f_2(s_2)}{kT} \right) \\ &\quad \exp \left(\frac{-\left(\hat{H}^N(q, \hat{p}'') + \frac{p_{N+2}^2}{2Q_2} - E\right)}{kT} \right). \end{aligned}$$

If we arrange that $g = M$ and that,

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

Then,

$$Z = \frac{K_2}{N!(N+1)kT} \int dp_{N+2} \int d\hat{p}'' \int dq \exp \left(\frac{-\left(\hat{H}^N(q, \hat{p}'') + \frac{p_{N+2}^2}{2Q_2} - E\right)}{kT} \right).$$

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

$$Z = \frac{C}{N!} \int dp'' \int dq \exp \left(\frac{-H(q, p'')}{kT} \right),$$

where,

$$C = \frac{2\pi K_2 \sqrt{Q_1 Q_2}}{N+1} \exp \left(\frac{E}{kT} \right),$$

and,

$$p'' = (p''_1, p''_2, \dots, p''_N).$$

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

III. NOSÉ CHAINS AND NOSÉ-POINCARÉ CHAINS.

f. In this section the application of multiple thermostats to both the Nosé and Nosé-Poincaré extended Hamiltonians is considered, in order to generate thermostating chains.

A. Nosé chains.

g. Thermostatting chains, consisting of M thermostats, can be added to the Nosé equation (1), with some additional terms as follows,

$$H^{NC} = H\left(q, \frac{p}{s_1}\right) + \sum_{i=1}^{M-1} \frac{p_{s_i}^2}{2Q_i s_{i+1}^2} + \frac{p_{s_M}^2}{2Q_M} + (N+1)kT \ln s_1 + \sum_{i=2}^M (kT \ln s_i + f_i(s_i)), \quad (14)$$

where the auxiliary functions $\{f_i(s_i)\}$ are real valued and satisfy,

$$\int_0^\infty \exp\left(\frac{-f_i(x)}{kT}\right) dx = K_i < \infty. \quad (15)$$

This extended system produces a canonical ensemble of $N + M$ degrees of freedom. The partition function for this ensemble, for energy E , is defined as,

$$Z = \frac{1}{N!} \int dp_{s_M} \dots \int dp_{s_1} \int ds_M \dots \int ds_1 \int dp \int dq \delta(H^{NC} - E). \quad (16)$$

We can substitute $p' = p/s_1$, the volume element then becomes $dp = s_1^N dp'$. There is no upper limit in momentum space so we can change the order of integration of dp' and ds_1 giving the integral over s_1 as,

$$\int ds_1 \delta(H^{NC} - E) = \int ds_1 s_1^N \delta\left(H(q, p', \hat{p}_s) + \sum_{i=2}^M F_i + (N+1)kT \ln s_1 - E\right),$$

where,

$$H(q, p', \hat{p}_s) = H(q, p') + \sum_{i=1}^{M-1} \frac{p_{s_i}^2}{2Q_i s_{i+1}^2} + \frac{p_{s_M}^2}{2Q_M}, \quad (17)$$

$$\hat{p}_s = \left(\frac{p_{s_1}}{s_2}, \dots, \frac{p_{s_{M-1}}}{s_M}, p_{s_M}\right), \quad (18)$$

and,

$$F_i = kT \ln s_i + f_i(s_i). \quad (19)$$

Using the equivalence relation for δ , $\delta(g(x)) = \delta(x - x_0)/|g'(x)|$, where x_0 is the zero of $g(x) = 0$, for $x = s_1$, and noting that $|s_1| = s_1$ since $\ln s_1$ is not defined for $s_1 < 0$, we get,

$$\int ds_1 s_1^N \delta\left(H(q, p', \hat{p}_s) + \sum_{i=2}^M F_i + (N+1)kT \ln s_1 - E\right)$$

$$\begin{aligned}
&= \int ds_1 \frac{s_1^{N+1}}{(N+1)kT} \delta \left(s_1 - \exp \left[\frac{-(H(q, p', \hat{p}_s) + \sum_{i=2}^M F_i - E)}{(N+1)kT} \right] \right) \\
&= \frac{1}{(N+1)kT} \exp \left[\frac{-(H(q, p', \hat{p}_s) + \sum_{i=2}^M F_i - E)}{kT} \right].
\end{aligned} \tag{20}$$

Substituting $p'_{s_1} = p_{s_1}/s_2$, changing the order of integration, and integrating (20) over s_2 we get,

$$\begin{aligned}
&\int ds_2 \frac{s_2}{(N+1)kT} \exp \left[\frac{-(H(q, p', p'_{s_1}, p_{s_2}, \dots, p_{s_M}) + \sum_{i=2}^M F_i - E)}{kT} \right] \\
&= \frac{K_2}{(N+1)kT} \exp \left[\frac{-(H(q, p', p'_{s_1}, p_{s_2}, \dots, p_{s_M}) + \sum_{i=3}^M F_i - E)}{kT} \right],
\end{aligned} \tag{21}$$

where K_2 is defined in (15). Repeating this for s_3, \dots, s_M gives,

$$\begin{aligned}
&\int ds_M \dots \int ds_1 \delta \left(H(q, p, \hat{p}_s) + \sum_{i=2}^M F_i + (N+1)kT \ln s_1 - E \right) \\
&= \frac{\prod_{j=2}^M K_j}{(N+1)kT} \exp \left[\frac{-(H(q, p', p'_{s_1}, p'_{s_2}, \dots, p'_{s_{M-1}}, p_{s_M}) - E)}{kT} \right].
\end{aligned} \tag{22}$$

Changing the order of integration and integrating (22) over all p'_{s_i} and p_{s_M} gives,

$$\begin{aligned}
&\int p_{s_M} \int p'_{s_{M-1}} \dots \int p'_{s_1} \frac{\prod_{j=2}^M K_j}{(N+1)kT} \exp \left[\frac{-(H(q, p', p'_{s_1}, \dots, p'_{s_{M-1}}, p_{s_M}) - E)}{kT} \right] \\
&= \frac{\pi^{\frac{M}{2}} (kT)^{\frac{M}{2}-1} \prod_{i=1}^M Q_i^{\frac{1}{2}} \prod_{j=2}^M K_j}{(N+1)} \exp \left[\frac{-(H(q, p') - E)}{kT} \right] \\
&= C_{NC} \exp \left[\frac{-H(q, p')}{kT} \right],
\end{aligned} \tag{23}$$

where,

$$C_{NC} = \frac{\pi^{\frac{M}{2}} (kT)^{\frac{M}{2}-1} \prod_{i=1}^M Q_i^{\frac{1}{2}} \prod_{j=2}^M K_j}{(N+1)} \exp \left(\frac{E}{kT} \right).$$

Then,

$$Z = \frac{C_{NC}}{N!} \int dp' \int dq \exp \left[\frac{-H(q, p')}{kT} \right]. \tag{24}$$

This means that constant energy dynamics of the extended Hamiltonian H^{NC} correspond to constant temperature dynamics of $H(q, p/s_1)$.

B. Nosé-Poincaré chains.

h. In a similar manner, thermostating chains, consisting of M thermostats, can be added to the Nosé-Poincaré equation (12), with some additional terms as follows,

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

where the auxiliary functions $\{f_i(s_i)\}$ are real valued and satisfy equation (15), and H_0 is equation (14) evaluated at the initial conditions. This extended system produces a canonical ensemble of $N + M$ degrees of freedom. The partition function for this ensemble is defined as,

$$Z = \frac{1}{N!} \int dp_{s_M} \dots \int dp_{s_1} \int ds_M \dots \int ds_1 \int dp \int dq \delta(H^{NPC} - 0). \quad (25)$$

Substituting $p' = p/s_1$, the volume element then becomes $dp = s_1^N dp'$. There is no upper limit in momentum space so we can change the order of integration of dp' and ds_1 giving the integral over s_1 as,

$$\int ds_1 \delta(H^{NPC}) = \int ds_1 s_1^N \delta \left(s_1 \left[H(q, p', \hat{p}_s) + \sum_{i=2}^M F_i + NkT \ln s_1 - H_0 \right] \right),$$

where $H(q, p', \hat{p}_s)$, \hat{p}_s and F_i are defined in equations (17)-(19). Using the equivalence relation for δ , $\delta(g(x)) = \delta(x - x_0)/|g'(x_0)|$, where x_0 is the zero of $g(x) = 0$, for $x = s_1$, to get,

$$\begin{aligned} \int ds_1 s_1^N \delta \left(s_1 \left[H(q, p', \hat{p}_s) + \sum_{i=2}^M F_i + NkT \ln s_1 - H_0 \right] \right) \\ = \int ds_1 \frac{s_1^N}{NkT} \delta \left(s_1 - \exp \left[\frac{-(H(q, p', \hat{p}_s) + \sum_{i=2}^M F_i - H_0)}{NkT} \right] \right) \\ = \frac{1}{NkT} \exp \left[\frac{-(H(q, p', \hat{p}_s) + \sum_{i=2}^M F_i - H_0)}{kT} \right]. \end{aligned}$$

The remaining thermostating variables can be integrated out as above in equations (21)-(24) to get the partition function,

$$Z = \frac{C_{NPC}}{N!} \int dp' \int dq \exp \left[\frac{-H(q, p')}{kT} \right], \quad (26)$$

where,

$$C_{NPC} = \frac{\pi^{\frac{M}{2}} (kT)^{\frac{M}{2}-1} \prod_{i=1}^M Q_i^{\frac{1}{2}} \prod_{j=2}^M K_j}{N} \exp\left(\frac{H_0}{kT}\right).$$

C. Auxiliary Function.

i. For the Nosé-chains to work correctly an auxiliary function, $f_i(s_i)$, must be chosen not only to satisfy equation (15) but to provide a suitable modification to the thermostats. One such choice is,

$$f_i(s_i) = \frac{(a_i - s_i)^2}{2C_i}, \quad (27)$$

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 of the form,

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

the equations of motion for s_i and p_{s_i} in the equivalent Nosé-chain system will be,

$$\begin{aligned} \dot{p}_{s_i} &= \frac{p_{s_{i-1}}^2}{Q_{i-1}s_i^3} - \frac{kT}{s_i} + \frac{a_i - s_i}{C_i}, \\ \dot{s}_i &= \frac{p_{s_i}}{Q_i s_{i+1}^2}. \end{aligned}$$

If C_i is sufficiently small, if s_i increases above a_i then p_{s_i} will decrease, eventually decreasing s_1 . Conversely, if s_i decreases below a_i then p_{s_i} will increase, eventually increasing s_1 .

D. Estimation of the Auxiliary Function Coefficient.

j. The value of C_i , $i \geq 2$ can be estimated by considering the equation of motion for the momenta of one of the thermostats, s_i ,

$$\dot{p}_{s_i} = \frac{p_{s_{i-1}}^2}{Q_{i-1}s_i^3} - \frac{kT}{s_i} + \frac{a_i - s_i}{C_i}. \quad (28)$$

Then the changes in s_i are 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 $\frac{ds_i}{dp_{s_i}}$ is a maximum at $s_i = a_i$. The negative feedback loops arising in Nosé dynamics drive $\langle \dot{p}_{s_i} \rangle$ to zero, in the

above equation, over a sufficiently long integration time. For the purpose of estimating the value of C_i , we will assume that \dot{p}_{s_i} is small. Then, from equation (28),

$$p_{s_{i-1}} \approx \sqrt{Q_{i-1} \left(kT s_i^2 - \frac{a_i s_i^3}{C_i} + \frac{s_i^4}{C_i} \right)}, \quad (29)$$

differentiating with respect to s_i ,

$$\frac{dp_{s_{i-1}}}{ds_i} \approx \frac{Q_{i-1} \left(2kT s_i - 3 \frac{a_i s_i^2}{C_i} + 4 \frac{s_i^3}{C_i} \right)}{2 \sqrt{Q_{i-1} \left(kT s_i^2 - \frac{a_i s_i^3}{C_i} + \frac{s_i^4}{C_i} \right)}}. \quad (30)$$

Differentiating again to get the turning points, and substituting $s_i = a_i$,

$$\frac{d^2 p_{s_{i-1}}}{ds_i^2} \approx \frac{Q_{i-1}^{\frac{1}{2}} a_i (8kT C_i - a_i^2)}{4(kT)^{\frac{3}{2}} C_i^2}. \quad (31)$$

Putting $\frac{d^2 p_{s_{i-1}}}{ds_i^2} = 0$ and solving for C_i gives,

$$C_i \approx \frac{a_i^2}{8kT}. \quad (32)$$

Evaluating $\frac{d^3 p_{s_{i-1}}}{ds_i^3}$ at this point gives a positive value, indicating a minimum for $\frac{dp_{s_{i-1}}}{ds_i}$ or a maximum for $\frac{ds_i}{dp_{s_{i-1}}}$ as required.

Experimental data from tests with the harmonic oscillator, with $a_i = 1$, show that Nosé chains will not work with $C_i > \frac{1}{8kT}$, but will work for all $C_i < \frac{1}{8kT}$. However, with very small values of C_i the additional thermostats become ineffective as s_i is restricted to a value close to 1.

IV. NUMERICAL EXPERIMENTS.

A. Hamiltonian Splitting Method.

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

$$H = \sum_{i=1}^N \frac{p_i^2}{2m_i} + V(q).$$

The Nosé-chains method derived from this, with M thermostats based on the auxiliary function in equation (27) is then,

$$H^{NC} = \sum_{i=1}^N \frac{p_i^2}{2m_i s_i^2} + V(q) + \sum_{j=1}^{M-1} \frac{p_{s_j}^2}{2Q_j s_{j+1}^2} + \frac{p_{s_M}^2}{2Q_M}$$

$$+NkT \ln s_1 + \sum_{j=2}^M \left(kT \ln s_j + \frac{(a_j - s_j)^2}{2C_j} \right),$$

giving a Nosé-Poincaré-chains method,

$$H^{NPC} = s_1 [H^{NC} - H_0],$$

where H_0 is chosen as the initial value of H^{NC} . The equations of motion are,

$$\begin{aligned} \dot{q}_i &= \frac{p_i}{m_i s_1}, & \dot{p}_i &= -s_1 \frac{\partial V(q)}{\partial q_i}, \\ \dot{s}_1 &= \frac{s_1 p_{s_1}}{Q_1 s_2^2}, & \dot{p}_{s_1} &= \sum_{i=1}^N \frac{p_i^2}{m_i s_1^2} - NkT \\ & & & - H^{NC}(q, \tilde{p}, s, p_s) + H_0, \\ \dot{s}_j &= \frac{s_1 p_{s_j}}{Q_j s_{j+1}^2}, & \dot{p}_{s_j} &= s_1 \left(\frac{p_{s_{j-1}}^2}{Q_{j-1} s_j^3} - \frac{kT}{s_j} + \frac{a_j - s_j}{C_j} \right), \\ & & & j = 2, \dots, M-1, \\ \dot{s}_M &= \frac{s_1 p_{s_M}}{Q_M}, & \dot{p}_{s_M} &= s_1 \left(\frac{p_{s_{M-1}}^2}{Q_{M-1} s_M^3} - \frac{kT}{s_M} + \frac{a_M - s_M}{C_M} \right), \end{aligned}$$

where $s = (s_1, \dots, s_M)$, $p_s = (p_{s_1}, \dots, p_{s_M})$ and $p = \tilde{p}/s_1$. 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 an odd number of thermostats, M , this can be reduced to three Hamiltonians by employing even-odd splitting of the extended variables. Then if,

$$H = H_1 + H_2 + H_3,$$

we have,

$$\begin{aligned} H_1 &= s_1 \left[\sum_{i=1}^N \frac{p_i^2}{2m_i s_1^2} + \sum_{i=1}^{\frac{M-1}{2}} \frac{p_{s_{2i}}^2}{2Q_{2i} s_{2i+1}^2} + NkT \ln s_1 \right. \\ &\quad \left. + \sum_{i=1}^{\frac{M-1}{2}} \left(kT \ln s_{2i+1} + \frac{(a_{2i+1} - s_{2i+1})^2}{2C_{2i+1}} \right) \right], \\ H_2 &= s_1 \left[\frac{p_{s_1}^2}{2Q_1 s_2^2} - H_0 \right], \\ H_3 &= s_1 \left[V(q) + \sum_{i=2}^{\frac{M-1}{2}} \frac{p_{s_{2i-1}}^2}{2Q_{2i-1} s_{2i}^2} + \frac{p_{s_M}^2}{2Q_M} \right] \end{aligned}$$

$$+ \sum_{i=1}^{\frac{M-1}{2}} \left(kT \ln s_{2i} + \frac{(a_{2i} - s_{2i})^2}{2C_{2i}} \right) \Bigg].$$

Using a symmetric splitting of the Liouville operator to get a symplectic and time reversible method,

$$\begin{aligned} iL_H = \{., H\} &= \{., H_1\} + \{., H_2\} + \{., H_3\} \\ &= iL_{H_1} + iL_{H_2} + iL_{H_3}. \end{aligned}$$

This splitting introduces an error of order Δt^3 at each step in terms of the solution operator, giving a second order method,

$$\begin{aligned} \Psi_H(\Delta t) &= e^{iL_H \Delta t}, \\ &= e^{iL_{H_3} \frac{\Delta t}{2}} e^{iL_{H_2} \frac{\Delta t}{2}} e^{iL_{H_1} \Delta t} e^{iL_{H_2} \frac{\Delta t}{2}} e^{iL_{H_3} \frac{\Delta t}{2}} \\ &\quad + O(\Delta t^3). \end{aligned}$$

The dynamics for H_1 and H_3 can be solved in a straightforward manner as each s_i and p_{s_i} are decoupled, leaving H_2 to be solved either analytically or by using the generalized leapfrog algorithm^{6,11}.

B. Harmonic Oscillator.

l. The Harmonic Oscillator is generally regarded as one of the hardest models to thermostat and as such is a good test for these methods. The Hamiltonian for the test system is,

$$H = \frac{p^2}{2m} + \frac{q^2}{2},$$

giving the Nosé-Poincaré-chains method,

$$\begin{aligned} H^{NPC} &= s_1 \left[\frac{p^2}{2m s_1^2} + \frac{q^2}{2} + \sum_{j=1}^{M-1} \frac{p_{s_j}^2}{2Q_j s_{j+1}^2} \right. \\ &\quad \left. + \frac{p_{s_M}^2}{2Q_M} + NkT \ln s_1 \right. \\ &\quad \left. + \sum_{j=2}^M \left(kT \ln s_j + \frac{(a_j - s_j)^2}{2C_j} \right) - H_0 \right]. \end{aligned}$$

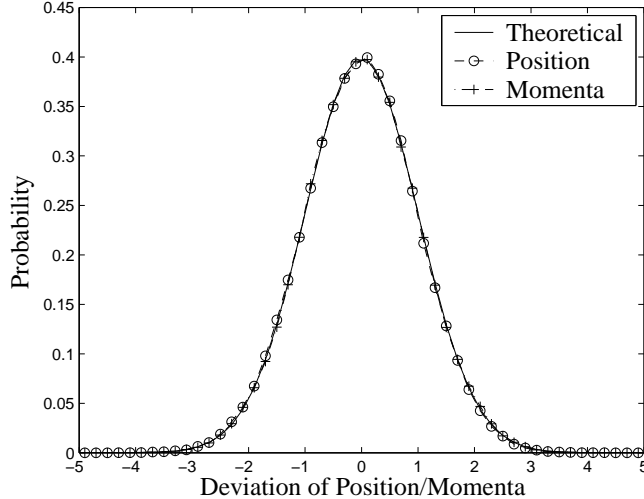


FIG. 1: Probability distribution for position/momenta. Optimum auxiliary function coefficients.

Using $\Delta t = 0.05$, $m = 1.0$, $Q_1 = 1.0$, $Q_2 = 3.0 \dots, Q_M = 3.0$, $C_2 = 0.08 = 1/12kT$, $C_3 = 0.04$, $C_4 = 0.02$, $C_5 = 0.01$, $kT = 1.0$, $M = 5$, $a_2 = \dots = a_M = 1$ produced good results with convergence close to the canonical distribution in 500,000 steps as shown in Figure 1.

To illustrate the importance of the correct selection of thermostating parameters, and the improvements obtained using thermostating chains, further experiments were carried out. When very small values are used for the C_i , the thermostats are forced to be close to 1, preventing them from operating and producing distributions that would normally be expected from the standard Nosé or Nosé-Poincaré methods, without thermostating chains, for the Harmonic oscillator. With the parameters the same as the above experiment except $\Delta t = 0.01$, $C_2 = 0.0008$, $C_3 = 0.0004$, $C_4 = 0.0002$, $C_5 = 0.0001$ gave the results in Figure 2.

As we can see from these examples, it is possible to choose thermostat masses to implement an efficient canonical sampling with the chain technique, while using symplectic integrators.

C. Estimating Thermostat Masses.

m. Values for the thermostating masses, Q_j , can be estimated by simplifying the equations of motion to decouple the thermostats, the resulting equations can then be linearized to evaluate their behavior near to a point of equilibrium. When calculating the masses for Nosé-Hoover chains⁸ it is assumed that adjacent thermostats are slow in compar-

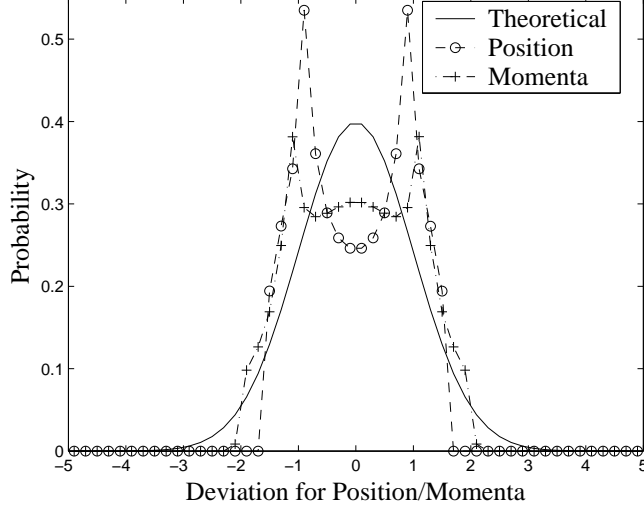


FIG. 2: Probability distribution for position/momenta. Small auxiliary function coefficients.

ison to the thermostat of interest, average values can then be used for $s_{j-1}, s_{j+1}, p_{s_{j-1}}, p_{s_{j+1}}$. Under these conditions, the analysis for the Nosé-Poincaré chains is similar to that provided by Nosé⁴ *provided that we also consider the variation in s_1 to be slow*, in order that we can replace it with its average value, for all but the first thermostat. For Nosé-Poincaré chains the equations of motion for s_j, p_{s_j} for $1 < j \leq M$ are,

$$\dot{s}_j = \frac{s_1 p_{s_j}}{Q_j s_{j+1}^2}, \quad (33)$$

$$\dot{p}_{s_j} = s_1 \left(\frac{p_{s_{j-1}}^2}{Q_{j-1} s_j^3} - \frac{kT}{s_j} + \frac{a_j - s_j}{C_j} \right). \quad (34)$$

Rearranging and differentiating (33), then substituting into (34),

$$\frac{d(Q_j s_{j+1}^2 \dot{s}_j)}{dt} = s_1^2 \left(\frac{p_{s_{j-1}}^2}{Q_{j-1} s_j^3} - \frac{kT}{s_j} + \frac{a_j - s_j}{C_j} \right). \quad (35)$$

We will consider a fluctuation δs_j of s_j around an average $\langle s_j \rangle$,

$$s_j = \langle s_j \rangle + \delta s_j. \quad (36)$$

Linearizing (35) to obtain an equation for δs ,

$$\begin{aligned} \frac{d}{dt}(Q_j s_{j+1}^2 \delta \dot{s}_j) = s_1^2 \left[\frac{p_{s_{j-1}}^2}{Q_{j-1} \langle s_j \rangle^3} \left(1 - 3 \frac{\delta s_j}{\langle s_j \rangle} \right) \right. \\ \left. - \frac{kT}{\langle s_j \rangle} \left(1 - \frac{\delta s_j}{\langle s_j \rangle} \right) \right. \\ \left. + \frac{a_j - \langle s_j \rangle - \delta s_j}{C_j} \right]. \end{aligned} \quad (37)$$

If the change in s_i is much faster than the rest of the system, then the change of the momentum can be ignored as the constant temperature is maintained by s_j , then,

$$\begin{aligned}\frac{p_{s_{j-1}}^2}{Q_{j-1}\langle s_j \rangle^3} &= \frac{kT}{\langle s_j \rangle} - \frac{a_j - \langle s_j \rangle}{C_j}, \\ &= \frac{kT}{\langle s_j \rangle},\end{aligned}\tag{38}$$

since a_j is chosen as $\langle s_j \rangle$, as discussed in section III C 0 i. Substituting (38) into (37), expanding the left hand side and substituting $\langle s_j \rangle = a_j$, $\langle s_{j+1} \rangle = a_{j+1}$, $s_1 \approx \langle s_1 \rangle$, we get,

$$\delta \ddot{s}_j = -\frac{\langle s_1 \rangle^2}{Q_j a_{j+1}^2} \left(\frac{2kT}{a_j^2} + \frac{1}{C_j} \right) \delta s_i,\tag{39}$$

giving a self-oscillation frequency, w_j , of,

$$w_j = \left(\frac{\langle s_1 \rangle^2}{Q_j a_{j+1}^2} \left(\frac{2kT}{a_j^2} + \frac{1}{C_j} \right) \right)^{\frac{1}{2}}.\tag{40}$$

Since we normally choose $a_j = 1$, $j \neq 1$, (40) reduces to the more general form,

$$w_j = \left(\langle s_1 \rangle^2 \left(\frac{2kT}{Q_j} + \frac{1}{Q_j C_j} \right) \right)^{\frac{1}{2}}.\tag{41}$$

For the remaining thermostat's variables, s_1 and p_{s_1} , the equations of motion are,

$$\dot{s}_1 = \frac{s_1 p_{s_1}}{Q_1 s_2^2},\tag{42}$$

$$\dot{p}_{s_1} = s_1 \left(\sum_{i=1}^N \frac{p_i^2}{m_i s_1^3} - \frac{NkT}{s_1} \right).\tag{43}$$

Following a similar procedure to that above gives a self-oscillation frequency, where $a_2 = 1$, of,

$$w_1 = \left(\frac{2NkT}{Q_1} \right)^{\frac{1}{2}},\tag{44}$$

which is of the form familiar from Nosé's paper⁴.

D. Optimum Thermostat Masses.

n. To evaluate the relationship between the self-oscillation frequencies and the optimum choice of the Nosé and auxiliary masses, experiments were carried out to assess the deviation from the required distribution with varying masses. The experiments were based

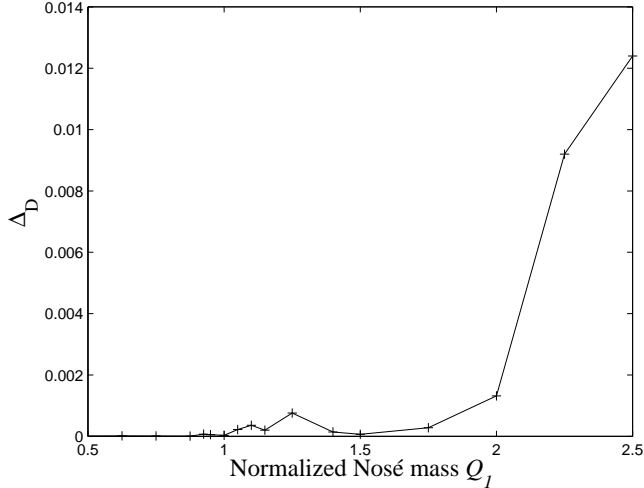


FIG. 3: Mean square deviation from the correct distribution with varying Nosé mass.

on the harmonic oscillator model with frequency 1.0, auxiliary function coefficient $C_2 = 0.08$, $a_2 = 1$, and having two thermostats, the original Nosé thermostat and one auxiliary thermostat. The initial conditions were chosen such that the average value of the Nosé variable s_1 was 1.0 and the results were taken after 5,000,000 steps, with a step size of 0.005.

In the first experiment the auxiliary thermostat mass was chosen to have a self-oscillation frequency equal to that of the harmonic oscillator and the Nosé thermostat was varied over a range of values, producing the results in figures 3 and 4. Here Q_1 has been normalized so that 1.0 is the value given by equation (44) and Δ_D represents the mean square difference between the actual and theoretical distributions. These indicate that the optimum choice of Nosé mass is near, but less than, its self-oscillation frequency, which is consistent with the results obtained for the auxiliary heat bath method⁹, but with good results for smaller values.

For the second experiment the Nosé mass was fixed at half that of its self-oscillation frequency and the mass of the auxiliary thermostat was varied, giving the results in figure 5. Here Q_2 has been normalized so that 1.0 is the value given by equation (41) and Δ_D is defined as above. From these results the optimum value for the auxiliary mass is around its self-oscillation frequency, but good results are obtained over a large range of values.

It should be noted that if equation (32) is satisfied then (41) reduces to,

$$w_j \approx \left(\langle s_1 \rangle^2 \frac{10kT}{Q_j} \right)^{\frac{1}{2}}. \quad (45)$$

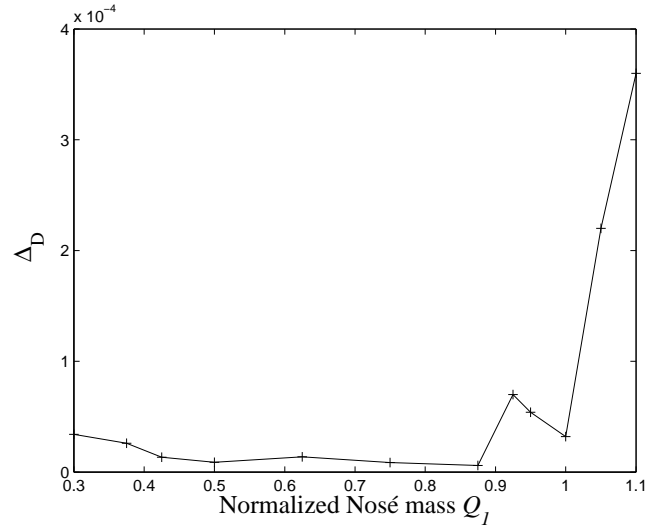


FIG. 4: Mean square deviation from the correct distribution with varying Nosé mass (expanded scale).

Acknowledgments

The authors wish to thank Brian B. Laird for his valuable comments and suggestions during the preparation of this paper. In addition the authors gratefully acknowledge support from the Engineering and Physical Sciences Research Council Grant. No. GR/R03259/01.

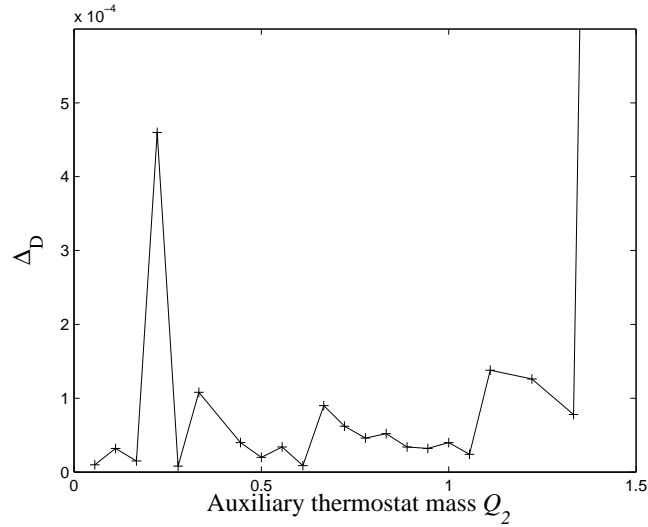


FIG. 5: Mean square deviation from the correct distribution with varying auxiliary thermostat mass.

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V. FIGURE CAPTIONS.

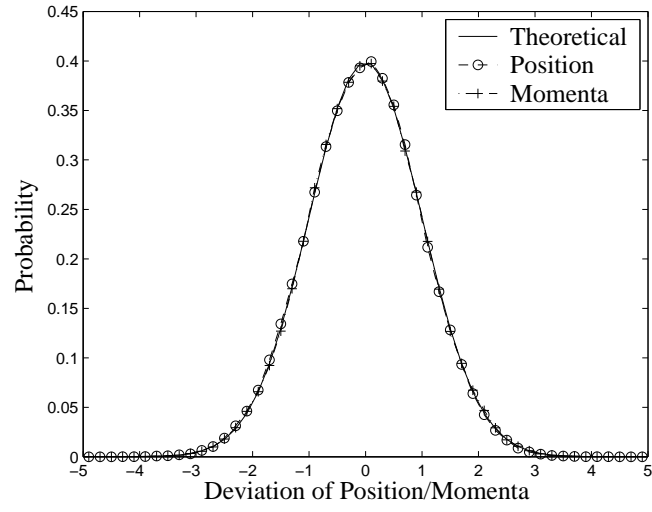
Figure 1: Probability distribution for position/momenta. Optimum auxiliary function coefficients.

Figure 2: Probability distribution for position/momenta. Small auxiliary function coefficients.

Figure 3: Mean square deviation from the correct distribution with varying Nosé mass.

Figure 4: Mean square deviation from the correct distribution with varying Nosé mass (expanded scale).

Figure 5: Mean square deviation from the correct distribution with varying auxiliary thermostat mass.



VI. FIGURES.

Figure 1:

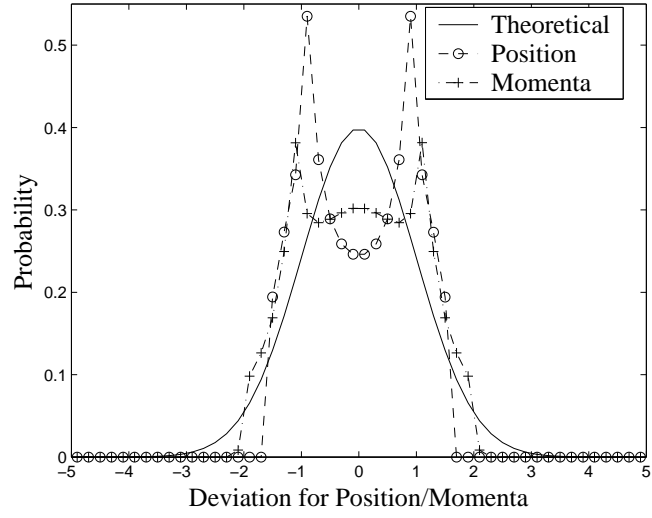


Figure 2:

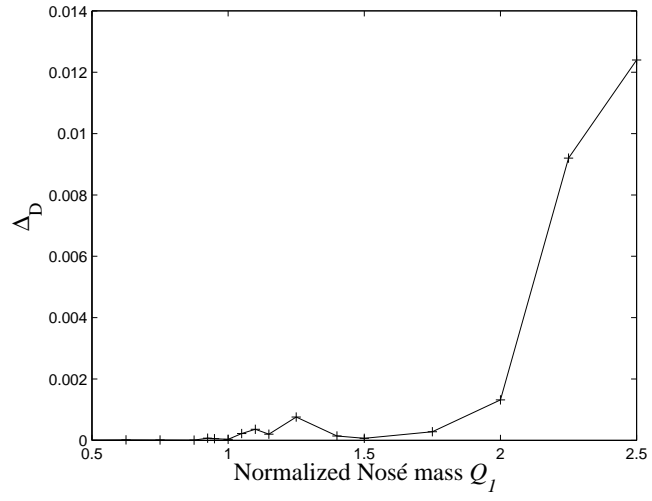


Figure 3:

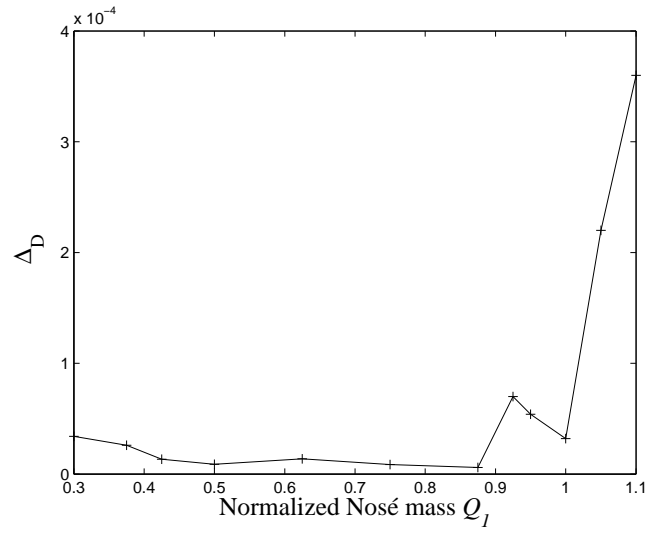


Figure 4:

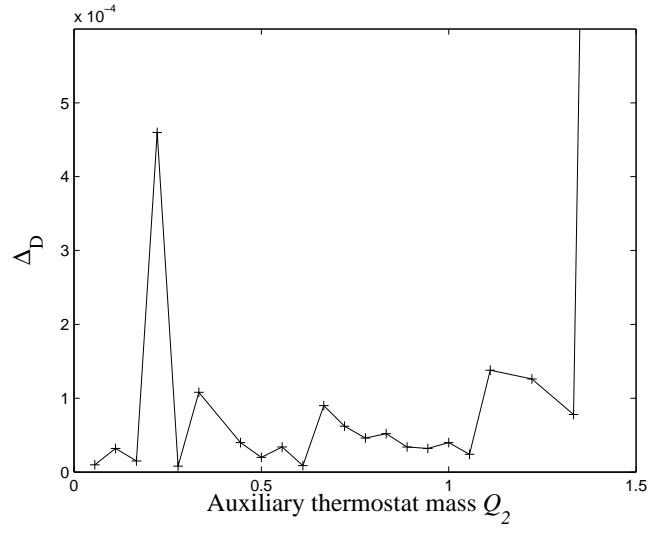


Figure 5: