

Non-Ergodicity of Nosé-Hoover Chain Dynamics

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ABSTRACT

Ergodicity of the dynamics is a prerequisite for obtaining ensemble averaged results from a single time trajectory, making it a key requirement for calculating statistical mechanical properties through molecular dynamics simulations. Nosé-Hoover chain (NHC) thermostat is a popular way of constraining temperature in molecular dynamics simulations. Previously, it was thought that NHC imparts ergodicity to the dynamics, thereby removing the deficiencies of several other thermostats. However, very recently, doubt has been casted on the ergodic nature of dynamics due to a two-chain NHC thermostat. In this work, we build upon this doubt and show, with the help of a single harmonic oscillator, that even after long time duration, the conditional univariate distribution functions of position and velocity do not reach a Gaussian distribution in several Poincare sections. The deviations from the Gaussian distribution are computed using the symmetric form of Kullback-Leibler divergence, Hellinger distance and by analysing the moments. The significant deviation of the conditional univariate distribution functions from a Gaussian distribution suggests that the dynamics due to NHC thermostat is non-ergodic although it constrains the temperature of the single harmonic oscillator to a desired value in a long time averaged sense.

Keywords: Molecular dynamics, Nosé-Hoover chains, Nonergodicity

1. INTRODUCTION

Thermostatting algorithms in molecular dynamics simulations provide us with the means of performing “numerical experiments” that have close resemblance to the “real life experiments” performed at constant temperature. Constant temperature (global and local) molecular dynamics has been used to calculate important transport properties like thermal conductivity [1, 2], diffusion constant [3, 4], viscosity [5] etc. for several systems. However, the ability of molecular dynamics to accurately evaluate these properties hinge on the ergodic nature of the dynamics [6]. In this context, the ergodic hypothesis may be stated as: given sufficiently long time, a single time trajectory would explore all the feasible regions of the phase space at a frequency in accordance with the theoretical probability distribution [7]. For constant temperature simulations, it means that the distribution function of position and velocity must follow the Gibbs distribution,

$$f(\mathbf{x}, \mathbf{p}) = \frac{1}{Z} \exp[-\beta H(\mathbf{x}, \mathbf{p})], \quad (1)$$

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where, \mathbf{x} and \mathbf{p} represent the position and the velocity of the particles, respectively. $H(\mathbf{x},\mathbf{p})$ is the energy of the system, $\beta = (k_B T)^{-1}$ and Z represents the partition function. A careful look at (1) suggests that the ergodic hypothesis may be loosely interpreted as phase-space filling nature of the dynamics [8].

There are several ways of imposing constant temperature in molecular dynamics simulations. These methods can be broadly grouped into three categories – velocity rescaling [4, 9-11], stochastic thermostats [12-14] and deterministic thermostats [15-22]. The earliest and simplest temperature control algorithms involved velocity rescaling, but these algorithms did not allow temperature fluctuations [23]. Amongst the three categories, only the deterministic thermostats have the appeal of being deterministic, unlike the stochastic thermostats, and are autonomous while simultaneously allowing temperature fluctuations.

Possibly, the best known deterministic thermostating technique is the Nosé-Hoover (NH) thermostat [15, 16] whose equations of motion are:

$$\dot{x}_i = p_i, \quad \dot{p}_i = -\frac{\partial\Phi(x_1, x_2, \dots, x_{3N})}{\partial x_i} - \eta p_i, \quad \dot{\eta} = \frac{1}{Q} \left[\sum_{i=1}^{3N} p_i^2 - 3Nk_B T \right]. \quad (2)$$

In (2), $\Phi(\cdot)$ represents the potential energy of the system. The NH thermostat works by controlling the second moment of velocity through the reservoir variable (η) whose mass is Q . If and only if the extended system is ergodic with respect to the invariant measure of the dynamics, the NH thermostat generates an ergodically consistent canonical distribution [23, 24]. Thus, only if the Gibbs distribution is satisfied, the underlying dynamics is ergodic.

It is interesting to note that the NH thermostat fails to provide a canonical distribution for a system comprising of a few particles, despite maintaining the temperature of the system at a desired value [25-30]. Over the years, investigations on lack of ergodicity of NH dynamics have been studied with a single harmonic oscillator, possibly because it is difficult to thermalize and yet is simple to analyse. For a single harmonic oscillator of unit mass at a desired temperature of 1 (with Boltzmann constant as unity), (2) may be written as:

$$\dot{x} = p, \quad \dot{p} = -x - \eta p, \quad \dot{\eta} = \frac{1}{Q} [p^2 - 1]. \quad (3)$$

The phase-space portrait of the dynamics for several initial conditions shows the presence of invariant tori, separating the phase-space into invariant regions [31]. Consequently, the resulting

dynamics fail to satisfy the Gibbs distribution (1). It has been argued that the equations of motion (3) lose their ergodic property due to the periodic dynamics of the thermostat variable and the presence of conserved quantities that cause the energy of the system to be bounded [29, 32]. The problem of nonergodicity is not limited to systems with lesser number of degrees of freedom and can manifest in multi-particle systems as well [32].

This inherent deficiency of NH thermostat is thought to be resolved by two methods – the kinetic moments method, that simultaneously controls of the second and the fourth moments of velocity [18] and the Nosé-Hoover chain (NHC) method [17], that controls the fluctuations of the thermostat variables. However, very recently doubt has been casted on whether the NHC thermostat indeed produces an ergodically consistent dynamics [7]. In this work, we build upon the nonergodicity of the NHC thermostatted dynamics by analysing the univariate conditional distribution functions of position and velocity for a single harmonic oscillator coupled with a two-chain NHC thermostat. Our results support the previous findings and show that the univariate conditional distributions have a significant deviation from a Gaussian distribution, and hence the dynamics is not ergodic. This paper is organized as follows: in the next section we detail the Nosé-Hoover chain thermostat followed by numerical results and conclusions.

2. THE NOSÉ-HOOVER CHAIN THERMOSTAT

The Nosé-Hoover chain (NHC) thermostat aims to remove the nonergodicity of the NH thermostat by additional control of the fluctuations of reservoir variable (η) through the second reservoir variable. The fluctuations of the second reservoir variable can likewise be controlled with the third reservoir variable and so on. Hence, a chain of thermostating variables is formed. The equations of motion of a k -chain NHC thermostat ($\eta_1, \eta_2, \dots, \eta_k$) coupled to a system comprising of N particles can be written as

$$\begin{aligned} \dot{x}_i &= p_i, & \dot{p}_i &= -\frac{\partial\Phi}{\partial x_i} - \eta_1 p_i, & \dot{\eta}_1 &= \left[\sum_{i=1}^{3N} p_i^2 - 3Nk_B T \right] - \eta_1 \frac{\eta_2}{Q_2}, \\ \dot{\eta}_j &= \left[\frac{\eta_{j-1}^2}{Q_{j-1}} - k_B T \right] - \eta_j \frac{\eta_{j+1}}{Q_{j+1}}, & \dots & & \dot{\eta}_k &= \left[\frac{\eta_{k-1}^2}{Q_{k-1}} - k_B T \right]. \end{aligned} \quad (4)$$

The variable η_i in (4) is associated with the i^{th} reservoir whose mass is Q_i . Empirical rule of selecting these thermostat masses is [17, 33]: $Q_1 = 3Nk_B T / \omega^2$ and $Q_{j \neq 1} = Nk_B T / \omega^2$. The

frequency, ω defines the oscillations of kinetic energy between the system and the reservoirs. This rule has many approximations inbuilt into it, and usually, a suitable choice of thermostat masses is problem dependent.

For the case of a single harmonic oscillator, having unit mass and spring constant, the equations of motion with two-chains (η and ξ) at $\beta = 1$, may be written as

$$\dot{x} = p, \quad \dot{p} = -x - \eta p, \quad \dot{\eta} = [p^2 - 1] - \eta \frac{\xi}{Q_\xi}, \quad \dot{\xi} = \left[\frac{\eta^2}{Q_\eta} - 1 \right]. \quad (5)$$

The equilibrium distribution due to NHC, if the ergodic property is satisfied for the extended system, can be written as

$$f(x, p, \eta, \xi) = \frac{1}{Z} e^{-\frac{1}{2}x^2} e^{-\frac{1}{2}p^2} e^{-\frac{1}{2Q_\eta}\eta^2} e^{-\frac{1}{2Q_\xi}\xi^2}. \quad (6)$$

In the past, it has been argued using numerical simulations that the equations of motion (5) is ergodically consistent and generates a distribution consistent with the extended Gibbs distribution (6). These studies had shown that the marginal velocity (and position) distribution, obtained by projecting the dynamics on to a particular position-velocity plane, has a Gaussian distribution, with the rationale being

$$f(p) = \int_{x, \eta, \xi} f(x, p, \eta, \xi) dx d\eta d\xi = \frac{1}{Z} e^{-\frac{1}{2}p^2}. \quad (7)$$

However, very recently it has been argued that the projected dynamics is incapable of capturing any inherent holes present in the phase space [7]. This is because (7) represents a necessary but not a sufficient condition for ergodicity to hold true. To illustrate this, we generated 1 million four dimensional (n_1 - n_2 - n_3 - n_4) joint standard normal data points, and then forcefully embedded a four dimensional hole of radius 0.25 in it. The projected dynamics along with the marginal distribution of n_1 and n_2 are shown in Figure 1. Neither the hole nor any deviations of the marginal distributions from a standard normal distribution could be observed. In fact, the first three marginal and the joint-moments of any two variables agree well with a standard normal distribution.

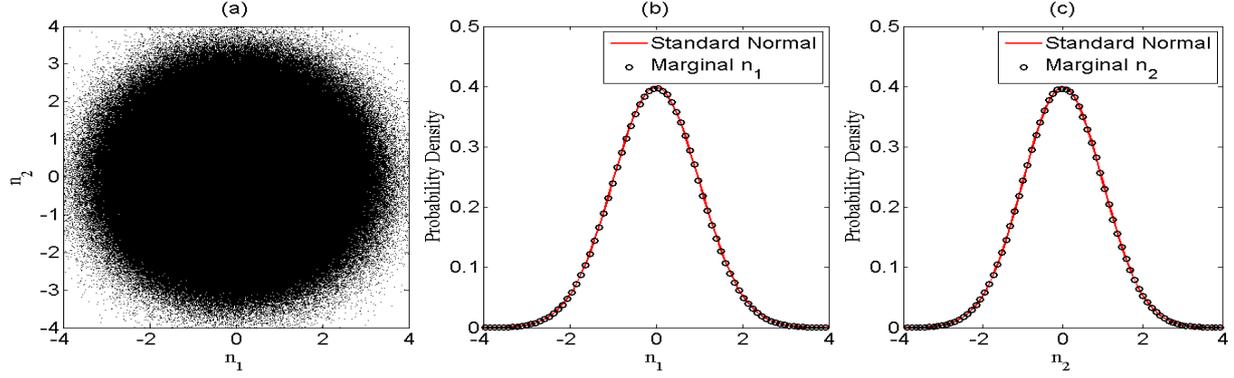


Figure 1. Inability of the projected dynamics to capture a forcefully embedded 4-dimensional hole of radius 0.25 within a four dimensional normally distributed data. The projected data is shown in the figure (a). Figures (b) and (c) plot the marginal distributions of the variables n_1 and n_2 . It can clearly be observed that these marginal distributions conform to a standard normal distribution without any deviation.

Possibly, a better and more stringent condition on ergodicity involves the conditional bivariate distribution of position and velocity,

$$f(x, p | \eta = \eta_0, \xi = \xi_0) = \frac{1}{Z''} e^{-\frac{1}{2}x^2} e^{-\frac{1}{2}p^2}. \quad (8)$$

In simpler terms, (8) means that the joint distribution of position and velocity must be jointly normal at every Poincaré section. Deviation of (8) from a joint normal distribution at any Poincaré section implies that (6) is not valid i.e. the dynamics does not sample canonical distribution correctly. Consequently, the dynamics must be nonergodic with holes of nonzero measure present in the phase-space. Recently, it has been shown that at several Poincaré sections (8) does not hold true [7].

In this article, we go a step further and analyse the univariate conditional distributions of position and velocity at a triple Poincaré section. Our method is based on the argument that if the position and velocity variables are statistically independent (as is generally assumed in equilibrium), a further stringent condition on ergodicity may be obtained by

$$\begin{aligned} f(x | p = p_0, \eta = \eta_0, \xi = \xi_0) &= \frac{1}{Z'''} e^{-\frac{1}{2}x^2}, \\ f(p | x = x_0, \eta = \eta_0, \xi = \xi_0) &= \frac{1}{Z'''} e^{-\frac{1}{2}p^2}. \end{aligned} \quad (9)$$

(9) is equivalent to saying that the conditional distribution functions of position at every triple Poincaré section defined by $p = p_0, \eta = \eta_0, \xi = \xi_0$ must be standard normal. Any deviation of LHS in (9) from a standard normal distribution implies that (8) is not satisfied which in turn suggests that (6) is incorrect. Thus, our method builds upon the recently suggested method [7]

and represents a more stringent criteria on proving (or disproving) the ergodicity of thermostatted dynamics. The aforementioned discussion is equally applicable for both the cases of same and different thermostat masses. In the next section we present our findings.

3. NUMERICAL SIMULATIONS AND RESULTS

We simulated the two-chain NHC thermostatted dynamics of a single harmonic oscillator at $k_B T = 1$ using four different thermostat masses: $(Q_\eta, Q_\xi) = (1, 1), (10, 0.1), (50, 0.02), (100, 0.01)$. We do not investigate the cases where $Q_\xi > Q_\eta$ since effective thermalization of the thermostat variable η can occur if $Q_\xi \leq Q_\eta$ i.e the relaxation time of the reservoir variable ξ is faster than η . The equations of motion (5) are integrated using a fourth order Runge-Kutta method for 200 billion time steps with each time step being equal to 0.001. Various initial conditions were chosen. The canonical nature of the dynamics was investigated by analysing the probability distributions of position and velocity (see (9)) at different Poincaré sections. The position-velocity plots in the some of the Poincaré sections investigated for the four different thermostat mass pairs are shown in Figure 2.

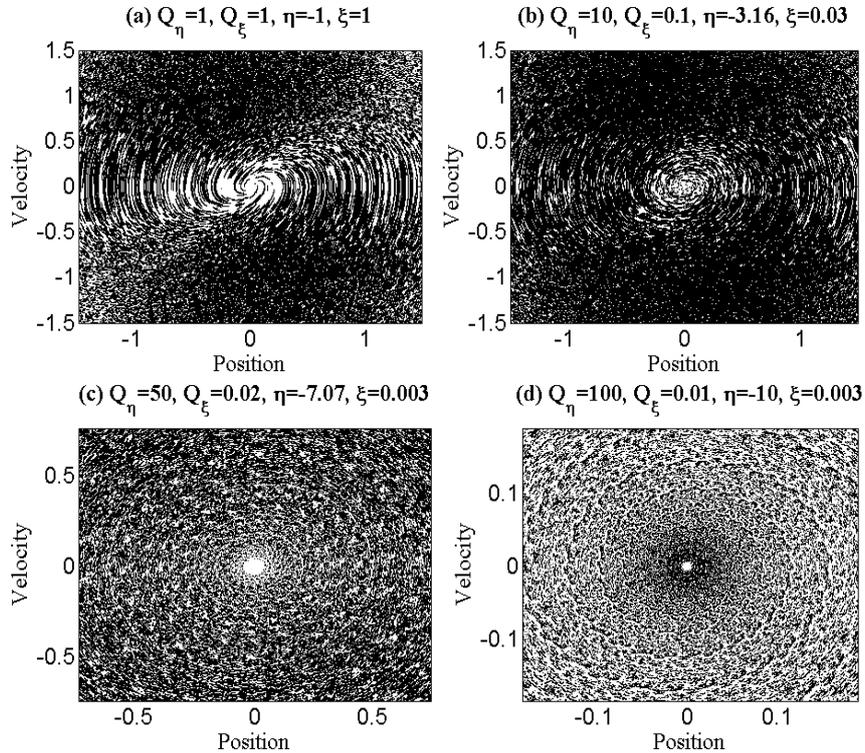


Figure 2. Position-velocity plots corresponding to different Poincaré sections for four different thermostat mass pairs. The system is initialized at $(x, p, \eta, \xi) = (1.1, 1.1, 0, 0)$. None of sections are consistent with ergodic dynamics. Presence of holes can be clearly seen.

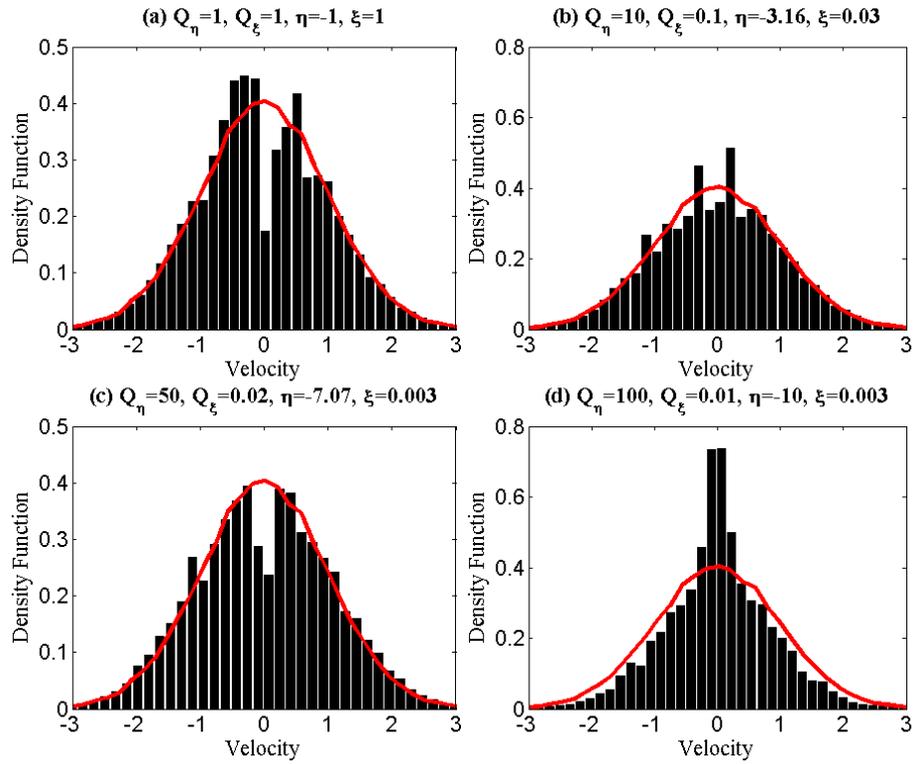


Figure 3. Univariate conditional distribution of velocity (black bars) as calculated according to (9). The red line represents a sample standard normal density function evaluated using 50,000 data points. Notice the mismatch between the black bars and the red line. For (a) and (c), there is a sudden dip of bars near origin, suggesting incorrect statistical sampling.

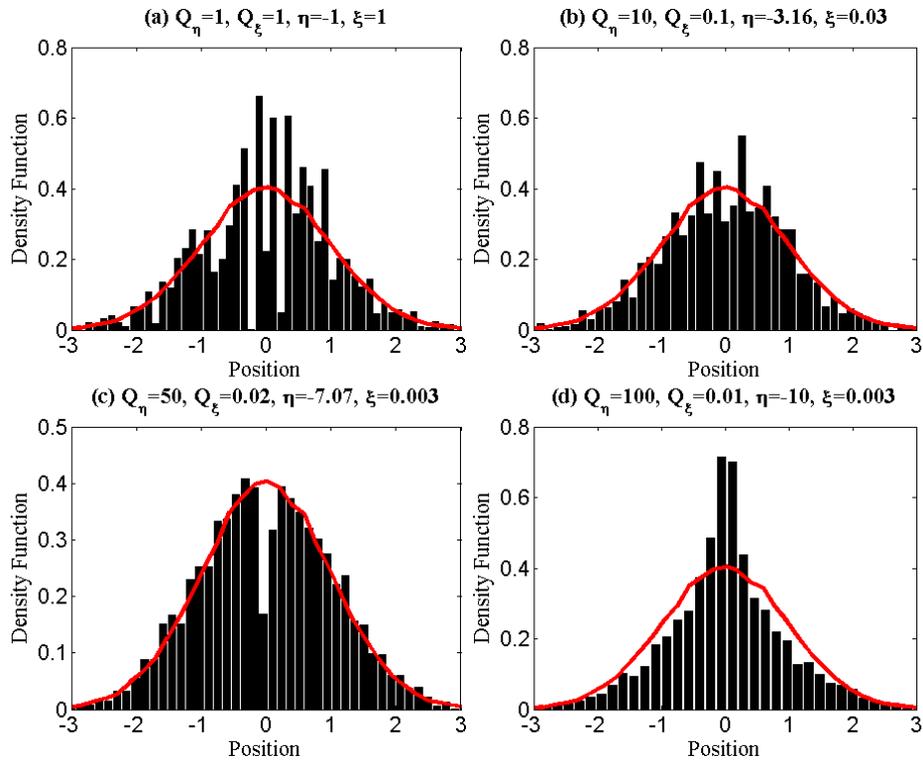


Figure 4. Univariate conditional distribution of position (black bars) as calculated according to (9). The red line represents a sample standard normal density function evaluated using 50,000 data points. Notice the mismatch between the black bars and the red line.

In the present work, we analyse the univariate conditional distribution of position and velocity for the data shown in Figure 2. A relatively wide slice (of width 0.1) has been considered at $x=0$ ($p=0$) for calculating the velocity (position) distribution function to compensate for the limited data points present in the double Poincaré section of Figure 2. The probability distributions (black bars) are plotted in Figure 3 and Figure 4. The red line indicates a standard normal density function evaluated using 50,000 simulated data points. It can clearly be observed that there is a substantial deviation between the black bars and the red line for each case, despite considering a considerably large slice. This, in turn, indicates that the LHS of (9) is not a standard normal, and hence, the dynamic is not ergodic.

The deviations from standard normal distribution are evaluated numerically through: Kullback-Leibler divergence [34] (D_{KL}) and Hellinger distance [35] (D_H):

$$D_{KL} = \sum_i f(i) \log \left[\frac{f(i)}{f_N(i)} \right],$$

$$D_H = \frac{1}{\sqrt{2}} \sqrt{\sum_i \left[\sqrt{f(i)} - \sqrt{f_N(i)} \right]^2}.$$
(10)

In (10), $f(i)$ is the relevant univariate distribution function and $f_N(i)$ is the corresponding standard normal distribution. Both the functions take a value 0 only if the two distributions are equal everywhere. The results are summarized in Table 1. It can be clearly observed that there is a significant deviation of the distribution functions from a standard normal distribution. Interestingly, the position distribution function shows a larger variation than the velocity distribution function.

Table 1. Kullback-Leibler divergence and Hellinger distance for the velocity and position distribution functions from a standard normal distribution. (Number#1,Number#2) in the second row indicates the value of the thermostat mass pair (Q_η, Q_ξ) . The deviation from the normal distribution is significant, especially for the position distribution function.

	Velocity Distribution Function				Position Distribution Function			
	(1,1)	(10,0.1)	(50,02)	(100,0.01)	(1,1)	(10,0.1)	(50,02)	(100,0.01)
D_{KL}	0.1281	0.0544	0.0865	0.3827	1.2000	0.1804	0.1443	0.3188
D_H	0.1837	0.1292	0.1552	0.3017	0.6378	0.2121	0.1995	0.2762

Next, we look at the first three even moments of position and velocity for the different thermostat masses. The results are summarized in Table 2. We again observe significant deviation in most of the cases from the moments of a standard normal distribution (second moment = 1.0, fourth

moment = 3.0 and sixth moment = 15.0). We again observe that the deviation from normal distribution is much more prominent for position distribution function than the velocity distribution function.

Table 2: The first three even order moments of position and velocity for different thermostat mass pairs (shown in second row). Notice the deviation from the correct value of moments for most of the cases.

	Velocity Distribution Function				Position Distribution Function			
	(1,1)	(10,0.1)	(50,0.2)	(100,0.01)	(1,1)	(10,0.1)	(50,0.2)	(100,0.01)
Second Moment	1.02	0.99	1.14	0.70	0.98	0.93	1.06	0.82
Fourth Moment	3.05	2.88	3.62	1.87	2.72	2.61	3.04	2.66
Sixth Moment	15.23	13.66	18.83	8.94	11.45	12.07	13.68	15.23

4. CONCLUSIONS

In this work, we built upon the recent doubt casted on the ergodicity of the Nosé-Hoover chain thermostatted dynamics. Using a single harmonic oscillator thermostatted at $k_B T = 1$, we have shown that the equations represented by (9) represent a much stronger criteria for proving (or disproving) the ergodicity of the dynamics. For the dynamics to be ergodic, (9) must be satisfied at every triple-Poincaré section. Any deviation of LHS from a standard normal distribution is an indicator of the underlying nonergodicity of the dynamics.

We show through numerical simulations, for both the equal and unequal thermostat mass cases, that the LHS of (9) does not indeed come from a standard normal distribution. The deviations from a normal distribution, as calculated using the Kullback-Leibler divergence, the Hellinger distance and the first three even order moments, are significant. These deviations are much more for the position distribution function than the velocity distribution function. Our results support the recent findings on the nonergodicity of the two-chain NHC thermostatted dynamics.

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