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An ergodic configurational thermostat using selective control of higher order temperatures

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The conventional Nosé-Hoover type deterministic thermostat scheme for controlling temperature by configurational variables (Braga-Travis (BT) thermostat) is non-ergodic for systems with a few degrees of freedom. While for the original Nosé-Hoover kinetic thermostat ergodicity has been achieved by controlling the higher order moments of kinetic energy, the issues of nonergodicity of BT thermostat persists. In this paper, we introduce two new measures of configurational temperature (second and third order) based on the generalized temperature-curvature relationship and obtain a family of deterministic thermostatting schemes by selectively (and simultaneously) controlling the different orders of temperatures through pseudo-friction terms. The ergodic characteristics of the proposed thermostats are tested using a single harmonic oscillator through statistical (normality of joint distributions at different Poincare sections) as well as dynamical tests (difference of the minimum and maximum largest Lyapunov exponent). Our results indicate that simultaneously controlling the first and the second order configurational temperatures ($C_{1,2}$ thermostat) is sufficient to make the dynamics ergodic. A 2000 particle Lennard-Jones system is subjected to (i) equilibrium and (ii) sudden temperature change under BT and $C_{1,2}$ thermostatting schemes. The $C_{1,2}$ thermostat is found to be more robust than the BT thermostat without increasing computational costs. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4921119]

I. INTRODUCTION

Molecular dynamics (MD) simulations have become indispensable for studying the physical properties of systems as different as proteins, fluids, crystals, etc. For an isolated system, classical MD samples the dynamics from an NVE ensemble constrained by constant linear momentum. Since physical processes typically take place with the system in contact with a heat reservoir, the equations of motion in MD need to be modified in a manner that energy exchange with external environment is allowed, and the dynamics samples from a canonical equilibrium distribution. To this end, several temperature control algorithms (or thermostats) have been introduced over the years. These algorithms may be classified into deterministic[1–10] and stochastic[11–14] algorithms. Until very recently, these thermostatting algorithms (whether deterministic or stochastic) were based on controlling only the kinetic temperature ($T_{\text{kinetic},1}$), defined through

$$T_{\text{kinetic},1} = \frac{2}{3Nk_B}\sum_{i=1}^{3N}\frac{p_i^2}{2m_i}. \tag{1}$$

However, the kinetic temperature based thermostats fail to perform satisfactorily in several nonequilibrium molecular dynamics (NEMD) situations. For example, in cases of flowing fluids, one needs to know the streaming velocity beforehand for calculating the peculiar kinetic energy, failing which unwanted effects, like stabilization of string phases, creep into the simulation.[15,16] For systems comprising of long molecules having several degrees of freedom, like proteins, thermostatting just the momentum variables is insufficient.[10] It has been shown through NEMD simulations that heat flux can be driven through a system in absence of any kinetic temperature gradient,[17,18] and the kinetic temperature, when used in Fourier's law, does not give accurate heat flux in systems with spatially varying shear rates.[19] These problems have stimulated the development of thermostats based on configurational temperature[20] ($T_{\text{config},1}$), defined through

$$T_{\text{config},1} = \frac{1}{k_B}\frac{\langle||\nabla_{r_i}\phi||^2\rangle}{\langle\nabla^2_{r_i}\phi\rangle}. \tag{2}$$

For reasons that will be clear later, we use the suffix 1 in (1) and (2). The equality of (1) and (2) in equilibrium makes it inconsequential as to which temperature is controlled under equilibrium conditions. This equality arises from the generalized temperature-curvature relationship[21] in equilibrium

$$\frac{1}{k_BT} = \frac{\langle\nabla.\nabla B\rangle}{\langle\nabla H.\nabla B\rangle}, \tag{3}$$

where B is an arbitrary scalar valued phase-function and T is the thermodynamic temperature. Substituting B as the kinetic energy $\sum p_i^2/2m_i$ gives (1) while substituting B as the potential energy, ϕ, gives (2). The real significance of configurational temperature arises in nonequilibrium cases, where the equality no longer holds true. For the purpose of controlling configurational temperature, several algorithms have been proposed

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in the literature.[10,22–24] Amongst them, the Braga-Travis (BT) thermostat[10] is probably the most popular. The BT thermostat controls $T_{\text{config},1}$ and is represented by

$$\dot{r}_i = \frac{p_i}{m_i} - \xi_1 \frac{\partial \phi}{\partial r_i}, \quad \dot{p}_i = -\frac{\partial \phi}{\partial r_i}, \\ \dot{\xi}_1 = \frac{1}{Q_{\xi_1}} \sum_{i=1}^{3N} \left[\left(\frac{\partial \phi}{\partial r_i} \right)^2 - k_B T \frac{\partial^2 \phi}{\partial r_i^2} \right]. \tag{4}$$

These equations have been derived using the extended-system method, first introduced by Nosé,[5,25] and then simplified by Hoover.[6] Like the Nosé-Hoover (NH) kinetic thermostat,[26] the BT thermostat suffers from poor ergodic characteristics for systems comprising of few degrees of freedom. For a single harmonic oscillator with unit spring constant and mass (including Q_{ξ_1}), and kept at $k_B T = 1$, (4) has the form

$$\dot{r} = p - \xi_1 r, \quad \dot{p} = -r, \quad \dot{\xi}_1 = r^2 - 1. \tag{5}$$

When solved using different initial conditions, (5) results in chaotic and regular solutions, with none of them satisfying the canonical distribution, for example, see Figure 1.

Ergodicity of dynamics is a prerequisite for estimating statistical-mechanical properties from a single dynamical trajectory observed over a sufficiently long period of time. The ergodic hypothesis enables us to equate the time average of a phase-function obtained from dynamical trajectories with its ensemble average

$$\langle h(r_i, p_i) \rangle_t = \langle h(r_i, p_i) \rangle_e, \tag{6}$$

where $h(r_i, p_i)$ is a phase-function, $\langle . \rangle_t$ is the time average, and $\langle . \rangle_e$ is its ensemble average. The definition of ergodicity chosen in the present article is similar to the Ehrenfests' quasiergodicity. Simply put, it means that a trajectory started from anywhere within the accessible phase-space eventually comes arbitrarily close to all microstates within the accessible region. The nonergodicity of the NH thermostat has been tackled by two methods: (i) the Nosé-Hoover chain (NHC) method[7] and (ii) the kinetic moments (HH) method.[8] NHC introduces additional (two or more) thermostat variables for controlling the fluctuations of preceding thermostat variables

$$\dot{r}_i = \frac{p_i}{m_i}, \; \dot{p}_i = -\frac{\partial \phi}{\partial r_i} - \frac{\eta_1}{Q_{\eta_1}} p_i, \\ \dot{\eta}_1 = (K - K_0) - \eta_1 \frac{\eta_2}{Q_{\eta_2}}, \; \dot{\eta}_2 = \frac{\eta_1^2}{Q_{\eta_1}} - \frac{2K_0}{3N}, \tag{7}$$

where K is the instantaneous kinetic energy: $K = \sum p_i^2 / 2m_i$, K_0 is the desired kinetic energy: $K_0 = 3N k_B T/2$, and Q_i are the thermostat masses. NHC dynamics shows apparent existence of holes in the Poincaré section near the fixed points[27] and fails to constrain temperature accurately out of equilibrium[28] where $\langle \eta_1 \eta_2 \rangle \neq 0$. Replacing η_1 with $\eta_1 - \langle \eta_1 \rangle$ in $\dot{\eta}_1$ and $\dot{\eta}_2$ equations of (7) improves the performance of the NHC thermostat in nonequilibrium cases[29] but adds to the computational burden as $\langle \eta_1 \rangle$ needs to be known in advance. The HH method[8] introduces two additive pseudo-friction thermostat variables for controlling the first two moments of the kinetic energy,

$$\dot{r}_i = \frac{p_i}{m_i}, \; \dot{p}_i = -\frac{\partial \phi}{\partial r_i} - \eta_1 p_i - \eta_2 \frac{K}{K_0} p_i, \dot{\eta}_1 = \frac{1}{Q_{\eta_1}} (K - K_0), \\ \dot{\eta}_2 = \frac{1}{Q_{\eta_2}} \left(K^2 - (1 + 2/3N) K K_0 \right), \tag{8}$$

and is known to impart ergodicity.[8,30]

But, unlike the NH dynamics, the nonergodicity of the BT dynamics for small systems still persists. An earlier attempt to develop an ergodic configurational thermostat[24] lacks the momentum evolution term and is stochastic in nature. In this paper, our objective is to develop new deterministic thermostatted equations for configurational degrees such that they have better ergodic characteristics than the BT equations. For this purpose, we introduce two new measures of configurational temperature ($T_{\text{config},2}$ and $T_{\text{config},3}$). These higher order configurational temperatures are simultaneously controlled using two new additive pseudo-frictional variables, akin to temperature control based on kinetic moments method (8). The new family of thermostats is first tested for ergodic characteristics using a single harmonic oscillator. Only those thermostats that show good ergodic characteristics are further subjected to performance comparison with the BT equations. For this purpose, we study a 2000 particle Lennard-Jones (LJ) system, first under

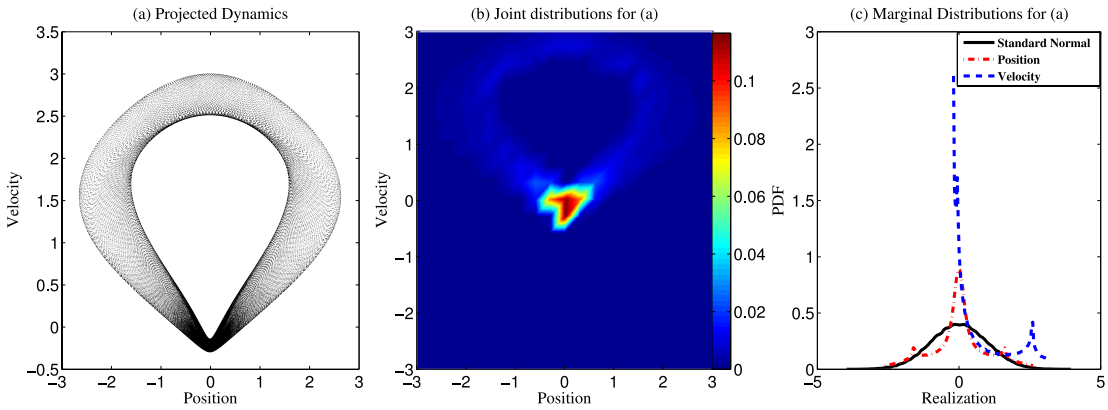

FIG. 1. Non-Ergodicity of the BT thermostatted single harmonic oscillator (5) kept at $k_B T = 1$: (a) phase-space plot (position-velocity) of the dynamics projected onto $\xi_1 = 0$ plane with the initial conditions $(r, p, \xi_1) = (2, 2, 1)$ solved using the fourth order Runge-Kutta method for 10×10^9 time steps, with $\Delta t = 0.001$, (b) joint distribution function of position and velocity, and (c) marginal distributions of position and velocity. The thermostat mass is taken as unity. It is evident from (a) that the dynamics is not phase space filling and is limited to a torus, and from (b) and (c), that the distribution is not canonical. Consequently, the BT dynamics is not ergodic for small systems.

equilibrium and then subjected to sudden temperature changes. Our results suggest that simultaneously controlling $T_{\text{config},1}$ and $T_{\text{config},2}$ is the most effective in improving the ergodic characteristics and at the same time is computationally as efficient as the BT thermostat.

II. NEW MEASURES OF CONFIGURATIONAL TEMPERATURE

Thermostats based upon standalone higher order kinetic temperatures obtained from higher moments of kinetic energy have been developed in the late 1980s,[31] but they also suffer from the problems of nonergodicity.[8] The first breakthrough in search for moments based ergodic thermostats came through the HH thermostat,[8] which simultaneously controls the temperatures corresponding to the first and the second moments of K according to (8). Recognizing that K is distributed according to χ^2 distribution, the kinetic temperature can be expressed in terms of the first two moments of K through

$$k_B T = \frac{\langle 2K^2 \rangle}{\langle K\,(3N+2) \rangle}. \tag{9}$$

The $\dot{\eta}_2$ equation of (8) controls precisely this temperature. It is interesting to note that one can find the same expression of temperature simply by substituting $B = K^2$ in (3).

In similar spirit, we introduce two new higher order measures of configurational temperature, which serve in modifying the BT equations of motion using general relation (3). Selecting $B = \phi^2$, we get the second order configurational temperature $T_{\text{config},2}$,

$$\frac{1}{k_B T_{\text{config},2}} = \frac{\langle ||\nabla_{r_i}\phi||^2 + \phi\nabla^2_{r_i}\phi \rangle}{\langle \phi ||\nabla_{r_i}\phi||^2 \rangle}, \tag{10}$$

and by selecting $B = \phi^3$, we get the third order configurational temperature, $T_{\text{config},3}$,

$$\frac{1}{k_B T_{\text{config},3}} = \frac{\langle 2\phi||\nabla_{r_i}\phi||^2 + \phi^2\nabla^2_{r_i}\phi \rangle}{\langle \phi^2 ||\nabla_{r_i}\phi||^2 \rangle}. \tag{11}$$

III. CONTROLLING HIGHER ORDER CONFIGURATIONAL TEMPERATURES IN SIMULATIONS

Proceeding along the lines of the kinetic moments based thermostat, we augment the BT dynamics by simultaneously and selectively controlling up to the third order configurational temperatures. One can use the same methodology for controlling even higher orders as well.

Let the contribution of the first three orders of the configurational temperature be embedded in the dynamics through the variables (ξ_1, ξ_2, ξ_3). The extended phase-space, therefore, comprises of the system and thermostat variables $(r_i, p_i, \xi_1, \xi_2, \xi_3)$. The coupling between the system variables (r_i, p_i) and the thermostat variables is sought to be of the form

$$\begin{aligned} \dot{r}_i &= p_i - \xi_1 \frac{\partial \phi}{\partial r_i} - 2\xi_2 \phi \frac{\partial \phi}{\partial r_i} - 4\xi_3 \phi^2 \frac{\partial \phi}{\partial r_i}, \\ \dot{p}_i &= -\frac{\partial \phi}{\partial r_i}, \\ \dot{\xi}_1 &= ?, \quad \dot{\xi}_2 = ?, \quad \dot{\xi}_3 = ?. \end{aligned} \tag{12}$$

For simplicity, we have assumed the mass of the particles to be unity.

Our objective is to find the time evolution of the thermostat variables such that the extended phase-space distribution becomes canonical in all variables, like as has been done for other cases,[9,10,32]

$$f \propto \exp\left[-\beta H - \sum_i \frac{1}{2} c_{\xi_i} \beta \xi_i^2 \right], \tag{13}$$

where $H = \phi + K$ and c_is are constants. To do so, the steady-state extended phase-space Liouville's equation is solved (assuming statistical independence of the variables),

$$\begin{aligned} &\frac{\partial f}{\partial t} + \sum_i \left(\dot{r}_i \frac{\partial f}{\partial r_i} + \dot{p}_i \frac{\partial f}{\partial p_i} \right) + \sum_j \dot{\xi}_j \frac{\partial f}{\partial \xi_j} \\ &\quad + f \left(\sum_i \left(\frac{\partial \dot{r}_i}{\partial r_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) + \sum_j \frac{\partial \dot{\xi}_j}{\partial \xi_j} \right) = 0. \end{aligned} \tag{14}$$

After simple algebraic manipulations, the governing equations become

$$\begin{aligned} \dot{r}_i &= p_i - \xi_1 \frac{\partial \phi}{\partial r_i} - 2\xi_2 \phi \frac{\partial \phi}{\partial r_i} - 4\xi_3 \phi^2 \frac{\partial \phi}{\partial r_i}, \\ \dot{p}_i &= -\frac{\partial \phi}{\partial r_i}, \\ \dot{\xi}_1 &= \frac{1}{Q_{\xi_1}} \sum_{i=1}^{3N} \left[\left(\frac{\partial \phi}{\partial r_i} \right)^2 - \frac{1}{\beta} \left(\frac{\partial^2 \phi}{\partial r_i^2} \right) \right], \\ \dot{\xi}_2 &= \frac{1}{Q_{\xi_2}} \sum_{i=1}^{3N} \left[\phi \left(\frac{\partial \phi}{\partial r_i} \right)^2 - \frac{1}{\beta} \left(\phi \frac{\partial^2 \phi}{\partial r_i^2} + \left(\frac{\partial \phi}{\partial r_i} \right)^2 \right) \right], \\ \dot{\xi}_3 &= \frac{1}{Q_{\xi_3}} \sum_{i=1}^{3N} \left[\phi^2 \left(\frac{\partial \phi}{\partial r_i} \right)^2 - \frac{1}{\beta} \left(\phi^2 \frac{\partial^2 \phi}{\partial r_i^2} + 2\phi \left(\frac{\partial \phi}{\partial r_i} \right)^2 \right) \right]. \end{aligned} \tag{15}$$

The variables Q_{ξ_i} can be viewed as mass of the ξ_ith reservoir variable. It is easy to check that these equations of motion constrain (2), (10), and (11). One can obtain a family of different thermostats from generalized equations (15) by controlling selectively (and simultaneously) the different degrees of freedom. For a single harmonic oscillator of unit mass, potential $\phi = 1/2r^2$, unit thermostat mass, and $\beta = 1$, (15) can be written as

$$\begin{aligned} \dot{r} &= p - \xi_1 r - \xi_2 r^3 - \xi_3 r^5, \dot{p} = -r, \\ \dot{\xi}_1 &= r^2 - 1, \dot{\xi}_2 = r^4 - 3r^2, \dot{\xi}_3 = r^6 - 5r^4. \end{aligned} \tag{16}$$

Equation (15) (and (16)) gives us the ability to control up to first three orders of configurational temperature simultaneously. We use the naming convention C_i for only the ith order configurational temperature control, $C_{i,j}$ for the simultaneous control of the ith and the jth order configurational temperatures, and $C_{1,2,3}$ for the simultaneous control of the first three orders of configurational temperature. Using this style, C_1 is identical to the BT thermostat. The C_i equations of motion are obtained by

substituting $\xi_{j\neq i} = \dot{\xi}_{j\neq i} = 0$ in (15). Similarly, $C_{i,j}$ equations are obtained by substituting $\xi_{k\neq i,j} = \dot{\xi}_{k\neq i,j} = 0$ in (15).

IV. ERGODICALLY THERMOSTATTING THE CONFIGURATIONAL VARIABLES

An ergodic dynamics must visit the neighbourhood of each and every allowable microstate, irrespective of the initial conditions, in same frequency as in the phase-space distribution. Ergodicity thus implies metric indecomposibility of the phase-space which in the context of canonical distribution requires space filling dynamics with no holes.[26] For the deterministic thermostats developed according to the extended system method (like the NH and BT thermostats), ergodicity is *assumed* in the extended phase-space in order to show that the dynamics samples from density function (13).

Ergodic properties of thermostatted dynamics are generally assessed using a single harmonic oscillator which is difficult to thermalize yet simple to analyze. It is easy to see from Figure 1 that BT dynamics violates the metric indecomposibility and does not satisfy Gibbs' distribution. However, for many-dimensional phase-space, it often becomes hard to locate the embedded holes from the projected dynamics, and ergodicity may be assessed by studying (i) the statistical properties of the phase variables and (ii) the Lyapunov exponents of the dynamics. The statistical approach is based on the property that the joint probability distribution of position and velocity (for single harmonic oscillator with $\phi = \frac{1}{2}r^2$) at fixed values of the reservoir variables is bivariate normal,[27]

$$f(r,p|\xi_i = \xi_{i,0}) \propto \exp\left[-\beta(\phi + K)\right] = \frac{1}{Z}\exp\left[-\frac{\beta}{2}(r^2 + p^2)\right]. \quad (17)$$

Any significant deviation of the LHS at any Poincare section (defined by $\xi_i = \xi_{i,0}$) from the joint normal distribution is an indication of nonergodicity of the dynamics. The second approach involves studying the difference between the maximum and minimum values of the largest Lyapunov exponents.[30,33] If the difference is large, then the dynamics is nonergodic. For an N-dimensional system, the Lyapunov spectrum may be obtained by solving $(N + 1)$ sets of N equations.[32] The first set of N equations is for the reference trajectory, while the remaining N sets (linearized equations of motion) describe the motion of the nearby satellite trajectories. After every iteration, the offset vectors are made orthonormal through the Gram-Schmidt orthonormalization procedure and are constrained to have a length of unity. Both these approaches are computationally expensive.

A. Nonergodicity of C_2 and C_3 controls

We have already shown that C_1 control, i.e., the BT thermostat is nonergodic (see Figure 1). In this section, we show that other controls of the type C_i (i.e., C_2 and C_3 controls) are nonergodic as well.

The C_2 control is run for several initial conditions using the fourth order Runge-Kutta method for 1×10^9 time steps with $\Delta t = 0.001$. The three-dimensional phase-space

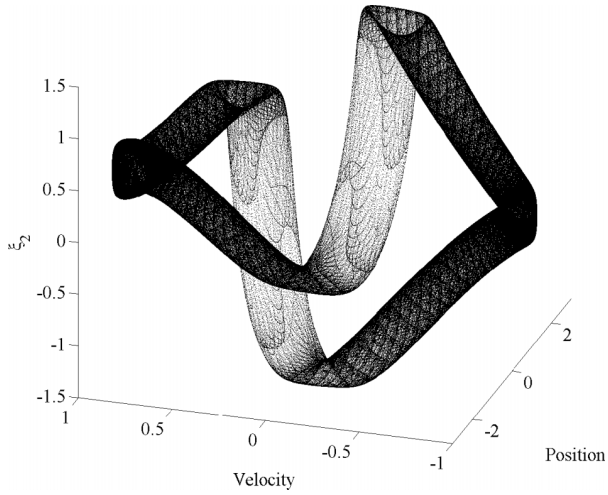

FIG. 2. Non-Ergodicity of the C_2 thermostatted single harmonic oscillator kept at $k_BT = 1$. The three-dimensional phase-space plot of the dynamics with initial conditions $(r, p, \xi_2 = -1.324\,684, -0.386\,117, -0.999\,791)$ shows that the dynamics is limited to a torus and does not explore the entire phase-space. Q_{ξ_2} is taken as unity. An ergodic thermostat must explore the entire phase space irrespective of the initial conditions, and thereby, we conclude that C_2 control is nonergodic.

plot with initial conditions $(r, p, \xi_2 = -1.324\,684, -0.386\,117, -0.999\,791)$ is shown in Figure 2. It is self evident that the dynamics is limited to a torus and is unable to explore the entire phase-space. Thus the C_2 control is non-ergodic. Of the 10 000 randomly chosen initial conditions, 1927 initial conditions resulted in regular trajectories with largest Lyapunov exponent insignificantly different from 0, which again confirms that C_2 is nonergodic.

We come to a similar conclusion for the C_3 control as well. Figure 3 shows the three-dimensional phase space plots with initial conditions $(r, p, \xi_3 = 1.560\,93, -0.604\,428, -1.743\,315)$ solved using the fourth order Runge-Kutta method for 1×10^9 time steps with each time step being equal to 0.0001. The dynamics remains confined to a torus and does not fill the entire phase-space. Of the 1000 randomly chosen initial conditions,

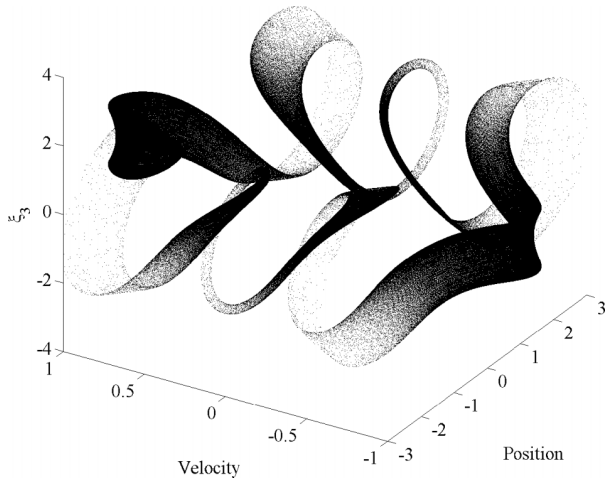

FIG. 3. Non-Ergodicity of the C_3 thermostatted single harmonic oscillator kept at $k_BT = 1$. The three-dimensional phase-space plot of the dynamics, with initial conditions $(r, p, \xi_3 = 1.560\,93, -0.604\,428, -1.743\,315)$ and unit Q_{ξ_3}, shows that the dynamics is limited to a torus, and like C_2 control, it does not explore the entire phase-space.

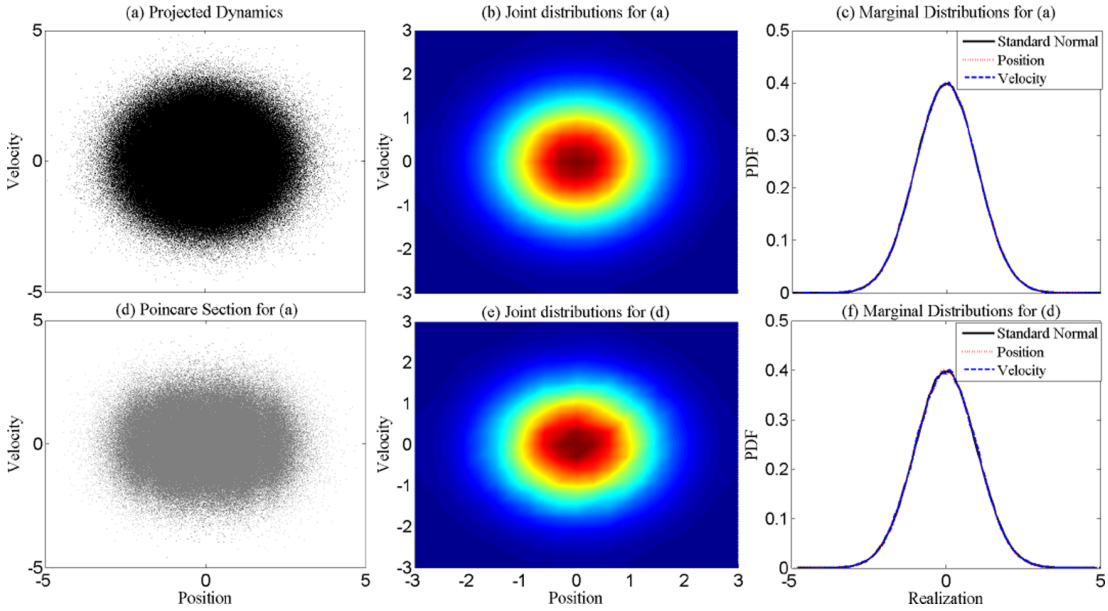

FIG. 4. Improved ergodic characteristics of the $C_{1,2}$ thermostatted single harmonic oscillator kept at $k_BT = 1$ with initial conditions $(r, p, \xi_1, \xi_2) = (2, 2, 1, 1)$ and unit values of Q_{ξ_i}. (a) denotes the plot of the projected dynamics while (d) denotes the corresponding Poincare section plot at $\xi_1 = 0$ and $\xi_2 = 0$ planes. The width of the Poincare sections is taken to be 0.0064. No existence of holes can be seen in any of these two cases. The dynamics that was previously limited to a torus (see Figures 1–3) now fills up the entire phase-space. Additionally, the joint distribution of position and velocity for both the cases is jointly normal (see (b) and (e)). The marginal distributions of position and velocities shown in (c) and (f) corresponding to (a) and (d), respectively, agree well with those of a standard normal distribution. Identical results were obtained with the initial conditions (5,5,5,5), (2,4,6,8), (1,0,0,0), and (1.5,3.0,4.5,6.0). The test for ergodicity at temperatures 2 and 3 also confirms that the dynamics samples from a normal distribution (with variances 2 and 3, respectively).

81 initial conditions resulted in regular trajectories with largest Lyapunov exponent insignificantly different from 0.

B. Improved ergodic characteristics of $C_{i,j}$ control

We begin with $C_{1,2}$ control. The equations of motion are solved using Runge-Kutta algorithm with $\Delta t = 0.001$ for 200×10^9 time steps. The projected phase space plots along with the Poincare section at the $(\xi_1, \xi_2) = (0, 0)$ plane are shown in Figure 4.

A comparison of Figures 1 and 4 suggests that the ergodic properties have improved greatly by simply controlling an additional temperature variable. The dynamics, which previously was limited to a torus, now fills up the entire phase space. Additionally, there is no existence of any unoccupied space (hole) in the dynamics at the Poincare sections. Also, the joint distributions of position and velocity obtained from both the projected dynamics (see Figure 4(b)) and at the Poincare section (see Figure 4(e)) show characteristic features of joint-normal distributions. Likewise, the marginal distributions (see Figures 4(c) and 4(f)) agree well with a standard normal distribution. An analysis of the first three even order joint and marginal moments of position and velocity for both the projected dynamics as well as the Poincare section suggests that (17) holds true. This concludes our assessment of ergodicity from the statistical perspective. We next move to the dynamical test for assessing ergodicity.

Table I shows the statistics of the Lyapunpov exponents obtained from 10 000 different initial conditions chosen randomly. The $C_{1,2}$ equations, for these cases, are solved for 2×10^6 time steps, each of size 0.005.

The minimum and maximum values of L_1 (see $L_1(\tau)$ column) obtained from these 10 000 points along with the initial conditions are shown in Table II. The trajectories corresponding to the maximum and minimum L_1 are evolved for further 10×10^6 time steps to check if they converge. The results indicate that they indeed converge (see $L_1(5\tau)$ column), suggesting that the dynamics is ergodic.

Thus, we see that due to additional control of $T_{\text{config},2}$, (i) the entire phase space gets filled, (ii) the distributions (marginal as well as joint) of position and velocity approach a Gaussian distribution, and (iii) there is no significant difference between the maximum and minimum values of L_1. We, therefore, conclude that the $C_{1,2}$ dynamics has much better ergodic characteristics than the original BT configurational thermostat. Similar arguments hold true for other two variable thermostats as well.

TABLE I. Lyapunov spectrum for the $C_{1,2}$ control. L_i denotes the ith Lyapunov exponent. The statistics are obtained using 10 000 randomly chosen initial conditions by solving for 2×10^6 time steps, each of size 0.005.

	L_1	L_2	L_3	L_4
Mean	0.0681	0.0026	−0.0054	−0.0695
Standard deviation	0.0034	0.0013	0.0013	0.0034

TABLE II. Minimum and maximum values of the largest Lyapunov exponent, L_1 along with their initial conditions obtained from 10 000 initially random points. Here, τ equals 2×10^6 time steps. It is evident that the minimum and the maximum L_1 approach each other as time increases.

	r	p	ξ_1	ξ_2	$L_1(\tau)$	$L_1(5\tau)$
Min	−0.220	−1.309	0.286	−1.747	0.056	0.065
Max	−0.273	−1.606	1.667	1.883	0.080	0.068

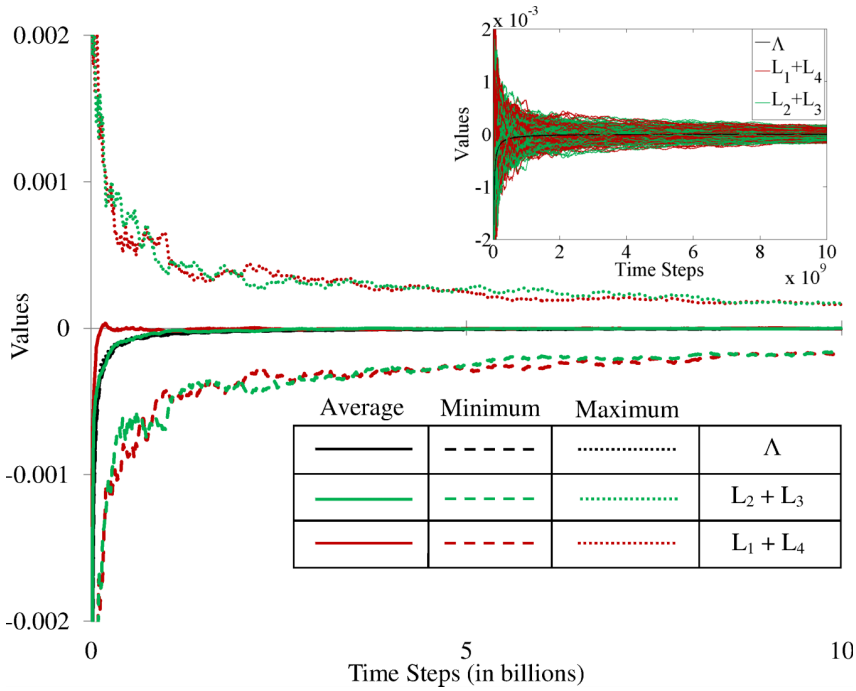

FIG. 5. The average (solid lines), minimum (big-dashed lines), and maximum (fine-dashed lines) of Λ, L_1+L_4, and L_2+L_3 calculated at each time instant from 150 initial conditions for the ergodic $C_{1,2}$ thermostat. All values clearly appear to converge to zero (the average dropping below 10^{-6} and the minimum/maximum dropping below 10^{-4} around 10×10^9 simulation steps). The inset shows temporal evolution of Λ, L_1+L_4, and L_2+L_3 for all of the 150 initial conditions. From the results, it is evident that the thermostat does no work on the system.

The $C_{1,2}$ thermostat derived in this study is non-Hamiltonian. Consequently, the phase-space compression (Λ) is not instantaneously zero even in equilibrium and is given by

$$\Lambda(t) \equiv \frac{\partial \dot{r}(t)}{\partial r(t)} = -\xi_1 \sum_{i=1}^{3N} \frac{\partial^2 \phi}{\partial r_i^2} - 2\xi_2 \sum_{i=1}^{3N} \left[\phi \frac{\partial^2 \phi}{\partial r_i^2} + \left(\frac{\partial \phi}{\partial r_i} \right)^2 \right]. \tag{18}$$

However, in a time averaged sense, there is no net compression/expansion of the phase-space, as should be in equilibrium,

$$\langle \Lambda \rangle_t \approx \langle \Lambda \rangle_e = -\langle \xi_1 \rangle_e \left\langle \sum_{i=1}^{3N} \frac{\partial^2 \phi}{\partial r_i^2} \right\rangle_e - 2\langle \xi_2 \rangle_e \left\langle \sum_{i=1}^{3N} \left[\phi \frac{\partial^2 \phi}{\partial r_i^2} + \left(\frac{\partial \phi}{\partial r_i} \right)^2 \right] \right\rangle_e = 0. \tag{19}$$

Here, we have used (6) and the independence of ξ_j with r_i. Recognizing that $\langle \xi_i \rangle_e = 0$, the last equality of (19) is obtained.

Phase space compression factor is intrinsically linked with the rate of change of Gibbs' entropy: $\dot{S} = k_B \langle \Lambda \rangle$. Λ, on the other hand, is related to the Lyapunov exponents through $\Lambda = \sum L_i$. Thus, we have $\dot{S} = \langle \sum L_i \rangle = 0$. Numerical results for a single harmonic oscillator (Figure 5) using 150 different initial conditions, each solved for 10×10^9 time steps (with a time step of 0.001), confirm that $\langle \sum L_i \rangle \approx 0$. Figure 5 shows the average, the minimum, and the maximum values of Λ, $L_1 + L_4$, and $L_2 + L_3$ at each time instant calculated using the 150 initial conditions. All values clearly appear to converge to zero (the average dropping below 10^{-6} and the minimum/maximum dropping below 10^{-4} around 10×10^9 simulation steps). Additionally, unlike the Gaussian iso-$K_{\mu+1}$ thermostats with $\mu > 1$,[34] for all initial conditions (i) $\sum L_i \approx 0$ (black lines in the inset of Figure 5) and (ii) the conjugate pairing rule: $L_1 + L_4 = L_2 + L_3 \approx 0$ (see the red and green lines of the inset) hold true in equilibrium. The lack of phase-space compression suggests that the thermostat forces do no work on the system.

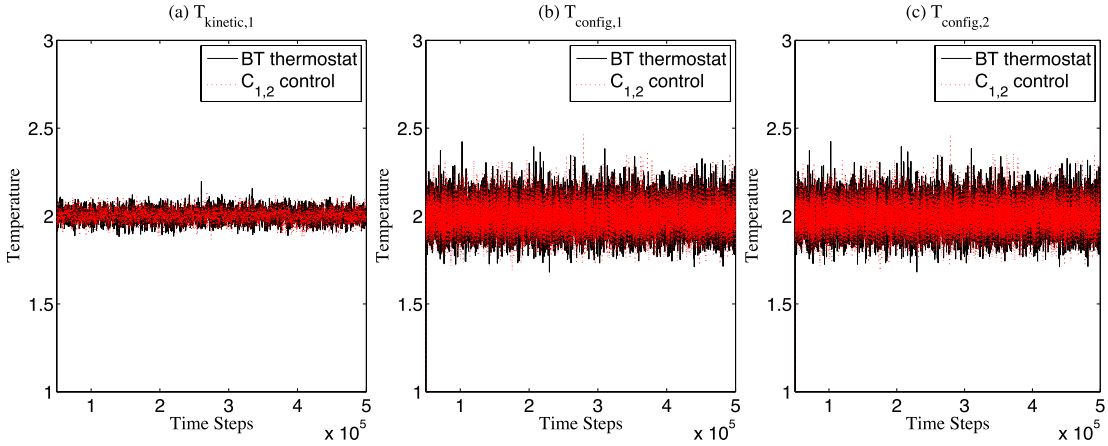

FIG. 6. Temperature time history for the BT thermostat (solid black lines) and the $C_{1,2}$ thermostat (dotted red lines) in equilibrium: (a) kinetic temperature ($T_{\text{kinetic},1}$), (b) first order configurational temperature, $T_{\text{config},1}$, and (c) second order configurational temperature $T_{\text{config},2}$. For both the thermostats, all three temperatures have similar mean as well as fluctuations out of mean.

TABLE III. Comparison of how well $C_{1,2}$ and BT thermostats control first order kinetic and the first and second order configurational temperatures at equilibrium. Mean (s.d.) computed from 10 000 equally spaced data points.

Thermostat	$T_{\text{kinetic},1}$	$T_{\text{config},1}$	$T_{\text{config},2}$
BT	2.004 (0.036)	1.999 (0.096)	2.000 (0.096)
$C_{1,2}$	2.003 (0.037)	1.999 (0.097)	1.999 (0.097)

We conjecture that, like the iso-$K_{\mu+1}$ thermostats, the configurational thermostats constructed through Gauss' principle of least constraint will show the unwanted feature of $\langle\Lambda\rangle \neq 0$.

V. COMPARISON FOR LARGE SYSTEMS

In this section, we compare the results of $C_{1,2}$ equations of motion with those of BT equations when thermostatting a relatively larger system. The system comprising of 2000 particles is subjected to two different cases—equilibrium and sudden temperature changes. The simulation domain is a periodic cube of edge length 14A. Initial particle positions and velocities are sampled from the uniform distribution and the Maxwell-Boltzmann distribution, respectively. Pairwise interaction ($\phi_{i,j}$) is taken as Lennard-Jones with a cut-off radius of 2.5,

$$\phi_{ij} = \begin{cases} 4\left[\left(\frac{1}{r_{ij}}\right)^{12} - \left(\frac{1}{r_{ij}}\right)^{6}\right] & r_{ij} \leq 2.5 \\ 0 & r_{ij} > 2.5 \end{cases}. \tag{20}$$

The system is equilibrated in two steps—first a conjugate gradient based energy minimization followed by 50 000 MD steps. We compute $T_{\text{kinetic},1}$, $T_{\text{config},1}$, and $T_{\text{config},2}$ for both the thermostats and in each case. After rigorous trial and error, we got $Q_{\xi_1} = 10^8$ and $Q_{\xi_2} = 10^{15}$ for a stable solution. Integration is performed using the modified velocity-Verlet algorithm with $\Delta t = 0.001$.

A. Equilibrium

This example has been designed to compare the performance of the $C_{1,2}$ control vis-a-vis the original BT equations.

TABLE IV. Comparison of CPU time needed for performing 100 000 MD runs.

	BT thermostat	$C_{1,2}$ control
CPU time (s)	1470	1475

The system has been thermostatted at a reduced temperature of 2. Post equilibration, the system is observed for 450 000 time steps. The temperature time-history of both the thermostats are shown in Figure 6.

A comparison of temperature statistics is shown in Table III. It is quite evident that both the thermostats perform comparably in equilibrium for constraining the mean temperature. In fact, the fluctuations for $C_{1,2}$ control is also similar to the BT control. However, we must point out that these fluctuations are dependent on the thermostat masses, Q_{ξ_i}, and tuning them could give smaller fluctuations. It is interesting to note that the instantaneous $T_{\text{config},2}$ follows $T_{\text{config},1}$ closely in both the cases and differs only at three digits post decimal, thus validating their equality in equilibrium. The central processing unit (CPU) time needed by the two thermostats is comparable as well. Table IV shows the time needed by both the methods. Notice that $C_{1,2}$ control is computationally as expensive as the BT thermostatted equations.

B. Sudden temperature changes

In this example, the system is subjected to sudden temperature changes twice: at $t = 500\,000\Delta t$, the reservoir temperature is doubled to 4, and at $t = 1\,000\,000\Delta t$, the reservoir temperature is halved to 2. The simulation is continued for another 500 000 time steps. This example tests the relative robustness of the proposed modifications, robustness being defined in terms of the time needed (t_{eq}) by the temperature fluctuations to reach an order of magnitude comparable to long-term fluctuations.[9]

Figure 7 shows the temperature time-history of both the thermostats in this case. Both the thermostats perform comparably, showing similar features. The time to equilibrate (t_{eq}) the system is shown in Table V. The equilibration time is

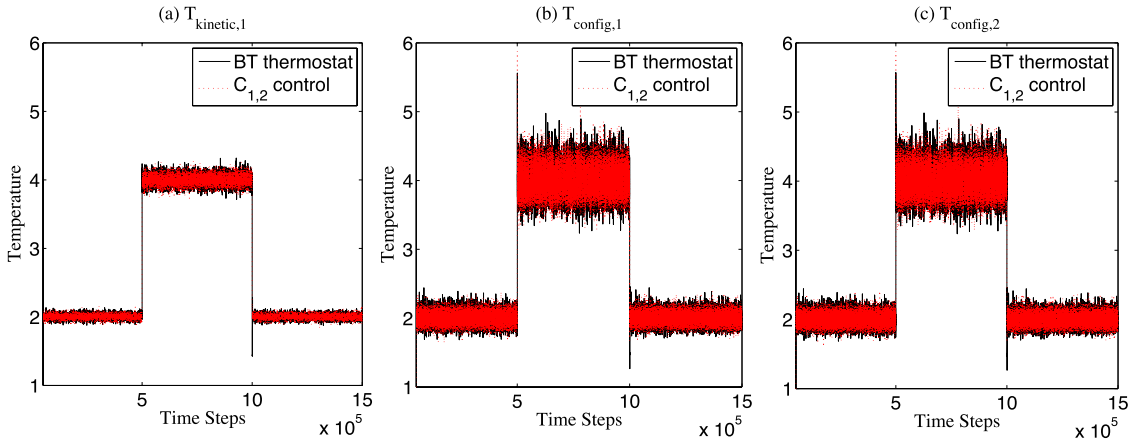

FIG. 7. Temperature time history for the BT thermostat (solid black lines) and $C_{1,2}$ thermostat (dotted red lines) due to sudden temperature changes: (a) kinetic temperature ($T_{\text{kinetic},1}$), (b) first order configurational temperature, $T_{\text{config},1}$, and (c) second order configurational temperature $T_{\text{config},2}$. After the first 500 000 time steps, the desired temperature is doubled to 4.0, which is again halved after 1 000 000 time steps. Both the thermostats perform comparably and have identical features.

TABLE V. Comparison of time steps needed for equilibration for both the thermostats (t_{eq}). The $C_{1,2}$ control is able to equilibrate the system faster in almost every case.

	$T_{\text{kinetic},1}$	
Thermostat	t_{eq} for first change	t_{eq} for second change
BT	2000	4000
$C_{1,2}$	3000	1200
	$T_{\text{config},1}$	
Thermostat	t_{eq} for first change	t_{eq} for second change
BT	1500	2000
$C_{1,2}$	1000	1000
	$T_{\text{config},2}$	
Thermostat	t_{eq} for first change	t_{eq} for second change
BT	1500	2000
$C_{1,2}$	1000	1000

calculated by dividing the temperature time-history data into bins of 200 post each change and then finding the first bin whose mean matches with the target temperature and subsequently stays within its 10%. The $C_{1,2}$ thermostat is able to equilibrate the system marginally faster than the BT thermostat in almost every case.

VI. CONCLUSION

The Braga-Travis configurational thermostat, despite its advantages, is nonergodic for small systems. In this work, we have introduced two new higher order configurational temperatures ($T_{\text{config},2}$ and $T_{\text{config},3}$) using the generalized temperature-curvature relationship and obtained a family of deterministic thermostatting schemes by selectively (and simultaneously) controlling these different orders of temperatures through pseudo-friction terms. The proposed modifications are subjected to rigorous tests for ergodicity first and then are assessed in their ability to control the configurational temperature of a realistic MD simulation.

We find that controlling just one measure, configurational temperature does not improve ergodicity. The fastest route to ergodicity is through the simultaneous control of $T_{\text{config},1}$ and $T_{\text{config},2}$. The resulting equations of motion are not computationally more expensive than the BT equations and retain the latter's benefits as well. They are robust, being able to equilibrate the system marginally faster than the BT thermostat during sudden temperature changes. However, it is possible that the best control would depend on the nature of the potential but we do not probe that angle further. We believe that the proposed equations would be useful in the different cases where BT thermostatted equations have been used.

The implementation of any configurational thermostat (including the BT thermostat) involves numerical calculation of higher derivatives of potential energy. This task is trivial for systems with simple pair-wise interaction having closed form function of potential energy. However, for a realistic system interacting through many-body potentials, implementing the configurational thermostats suffers from significant increase in computational resources, limiting their utility. Development of better and faster algorithms for calculating these higher order derivatives would significantly benefit the adoption of configurational thermostats in simulations.

In closing, we would like to point out that the thermostats employed in molecular dynamics, be it kinetic or configurational, are artificial mechanisms for modeling what occurs in nature.[35] It therefore makes sense to develop a range of thermostatting mechanisms and understand which of them can accurately describe the problem of interest. While it is known that for large systems the issue of ergodicity is irrelevant (since the Poincaré recurrence time is greater than the age of universe), the issue at hand is the reproducibility of natural processes. Recent developments indicate that the dynamical processes of systems in nonequilibrium are dependent on the thermostat algorithm.[36] It still remains unknown whether using ergodic thermostats (like the kinetic-moments method and the proposed method) would result in different dynamical properties in comparison to those obtained from nonergodic thermostats (like the NH and BT) for nonequilibrium cases.

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