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# A deterministic thermostat for controlling temperature using all degrees of freedom

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We propose a new thermostat that uses all the phase space variables for controlling temperature and thus differs from the existing thermostats that control either the kinetic (e.g., Nose Hoover) or the configurational (e.g., Braga Travis) degrees of freedom. Our thermostat is a special case of the set of equations proposed by Kusnezov *et al.* [Ann. Phys. **204**, 155 (1990)] and is derived using the extended system method. We show that it generates a canonical phase-space distribution. The performance of the thermostat is compared with those of Nose-Hoover kinetic thermostat and Braga-Travis configurational thermostat for a system (i) in thermal equilibrium, (ii) subjected to sudden temperature changes, and (iii) in steady state non-equilibrium under thermal conduction. We observe that all three thermostats perform similarly for systems in equilibrium. However, our thermostat performs the best in the thermal conduction problem by generating a consistent temperature profile across the conduction length. We expect this thermostat to be useful in other non-equilibrium scenarios as well. (© 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4864204]

#### I. INTRODUCTION

An isolated system in a 6N dimensional phase space  $(r_1, r_2, \ldots, r_{3N}, p_1, p_2 \ldots, p_{3N})$ , whose Hamiltonian is given by *H*, is governed by the usual Hamilton's equations of motion (EOM):

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m_i} + \phi(r_1, r_2, \dots, r_{3N}),$$

$$\frac{dr_i}{dt} = \frac{\partial H}{\partial p_i},$$

$$(1)$$

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial r_i}.$$

When an external force performs work on this system at a finite rate, heat is produced and the system is driven out of equilibrium.<sup>1</sup> If one wishes to generate a steady-state it becomes mandatory to extract this heat using some kind of a thermostat which keeps the temperature constant throughout the simulation. Until very recently, this was achieved by controlling just the kinetic part of the temperature<sup>2</sup> which can be expressed using the equipartition theorem through the relation:

$$T_{kinetic} = \frac{2}{3Nk_B} \sum_{i=1}^{3N} \frac{p_i^2}{2m}.$$
 (2)

The first attempts of constant temperature molecular dynamics simulations involved maintaining the instantaneous kinetic temperature of the system at the desired value without any allowance for fluctuations.<sup>3–5</sup> Over the years several other deterministic<sup>6–13</sup> and stochastic<sup>14,15</sup> thermostats have been developed by constraining  $T_{kinetic}$ . However, controlling the kinetic part of temperature alone may not be adequate for simulating certain heat driven non-equilibrium molecular dynamics simulations<sup>16,17</sup> and simulations involving very long molecular systems (e.g., polymers and proteins). The difficulty of  $T_{kinetic}$  based temperature control in flowing non-equilibrium systems with spatial and possibly time varying streaming velocity<sup>18,19</sup> actually was a driver for the development of configurational thermostats, as discussed next.

Some of the problems associated with controlling kinetic temperature can be alleviated with thermostats based on controlling the configurational part of the temperature<sup>20–25</sup> which constrain the configurational variables of the system. Temperature when expressed through configurational variables is

$$T_{config} = \frac{1}{k_B} \frac{\|\nabla_r \phi\|^2}{\nabla_r^2 \phi}.$$
(3)

For an equilibrium system, given sufficient time, controlling the kinetic part of the temperature would control the configurational part of the temperature and vice versa. The proof is due to the works of Rugh<sup>26</sup> and Butler *et al.*<sup>27</sup> The general relationship of temperature with an arbitrary phase-space function (*B*)<sup>28</sup> can be written as

$$\frac{1}{k_B T} = \frac{\left\langle \nabla_r^2 B + \nabla_p^2 B \right\rangle}{\left\langle \|\nabla_r B\|^2 + \|\nabla_p B\|^2 \right\rangle} = \lim_{t \to \infty} \frac{1}{t} \int_0^t \left( \nabla \cdot \frac{\nabla B}{\|\nabla B\|^2} \right) d\tau,$$
(4)

the RHS being valid under the assumption of ergodicity. Equations (2) and (3) can be obtained from (4) through appropriate selection of *B*. Choosing *B* as the potential energy ( $\phi$ ) leads to (3), choosing *B* as the kinetic energy (*K*) leads

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to (2). Setting *B* equal to *H* in (4) leads to Rugh's temperature,  $T_{Rugh}$ :

$$\frac{1}{k_B T_{Rugh}} = \frac{\left\langle \sum_{i=1}^{3N} \frac{1}{m_i} + \nabla_r^2 \phi \right\rangle}{\left\langle \sum_{i=1}^{N} \left( \frac{p_i}{m_i} \right)^2 + \|\nabla_r \phi\|^2 \right\rangle} = \lim_{t \to \infty} \frac{1}{t} \int_0^t \left( \nabla \cdot \frac{\nabla H}{\|\nabla H\|^2} \right) d\tau.$$
(5)

The RHS again being valid under ergodicity. These definitions of temperature are valid in the canonical as well as molecular dynamics ensembles. As said before, at equilibrium the three temperatures are equal:

$$T_{Rugh} = T_{config} = T_{kinetic}.$$
 (6)

Importantly, (6) does not generally hold true for nonequilibrium systems unless they satisfy local thermal equilibrium (LTE).<sup>29–31</sup> Consequently, the dynamical properties of a non-equilibrium system show dependence on thermostatting scheme<sup>32</sup> and leave us with the question which temperature should be controlled when simulating non-equilibrium steady states. For example, when shear rate tends to zero, the first normal stress coefficients of shearing fluids show a significant dependence on the definition of the temperature being controlled.<sup>33</sup> The kinetic and configurational temperature profiles are significantly different for  $\phi^4$  chains when the two ends are thermostatted at different temperatures using either kinetic or configurational thermostats.<sup>34–36</sup> As we also show later in this paper that despite the existence of local thermal equilibrium, temperature profiles obtained along the direction of thermal conduction are dependent on the choice of thermostatting scheme. These highlight the necessity of developing a thermostat that can control both the kinetic and configurational temperatures and not just either one of them.

In this work, we propose a new thermostat that differs from the existing ones by utilizing the entire phase space variables for controlling temperature. The thermostat is derived using extended system method and generates a unique canonical phase-space distribution. We compare the performance of our thermostat with Nose-Hoover (NH) kinetic thermostat and Braga-Travis (BT) configurational thermostat. The NH thermostat is the simplest amongst the thermostats that controls the kinetic temperature efficiently for all but small or stiff systems, and is the basis for most of the canonical dynamics proposed in the literature<sup>37</sup> and BT thermostat is a generalized form for controlling configurational temperature,<sup>38</sup> and has seen wide acceptance.<sup>39-42</sup> We show that the proposed thermostat performs better than NH and BT thermostats in simulating a non-equilibrium phenomenon like thermal conduction by generating a consistent temperature profile across the conduction length. The paper is organized as follows – in Sec. II we give a brief description of methods of generating canonical dynamics. After that, we derive the proposed thermostat, following which simulation results and comparison with other thermostats are presented.

# II. THE EXTENDED-SYSTEM METHOD

The system is augmented by artificial degrees of freedom (dof) and their conjugates to account for the effects of the

reservoir.<sup>43</sup> Both the NH kinetic thermostat and BT configurational thermostat are examples of this method. Extended system dynamics can be developed using two approaches.<sup>37</sup> One can begin with the extended system Lagrangian and then perform a variable transformation of the equations of motion.<sup>6</sup> Alternatively, the EOM are guessed (guessing method) and then the coupling coefficient is decided in such a way that a canonical ensemble is obtained.<sup>8, 12, 44, 45</sup> To develop the NH thermostat,<sup>7</sup> one guesses the first two equations of (7) and then arrives at the time evolution of coupling coefficient ( $\dot{\eta}$ ) by solving the steady state extended Liouville's equation:

$$\dot{r}_{i} = \frac{p_{i}}{m_{i}},$$

$$\dot{p}_{i} = -\frac{\partial \phi}{\partial r_{i}} - \eta p_{i},$$

$$\dot{\eta} = \frac{1}{Q_{NH}} \left[ \sum_{i=1}^{N} \frac{p_{i}^{2}}{m} - 3Nk_{B}T_{0} \right].$$
(7)

Similarly for BT thermostat,<sup>22</sup> the first two equations of (8) are guessed and then the time evolution of the coupling coefficient ( $\dot{\xi}$ ) is derived:

$$\begin{aligned} \dot{r}_{i} &= \frac{p_{i}}{m_{i}} - \xi \frac{\partial \phi}{\partial r_{i}}, \\ \dot{p}_{i} &= -\frac{\partial \phi}{\partial r_{i}}, \\ \dot{\xi} &= \frac{1}{Q_{BT}} \sum_{i=1}^{3N} \left( \beta \left( \frac{\partial \phi}{\partial r_{i}} \right)^{2} - \frac{\partial^{2} \phi}{\partial r_{i}^{2}} \right). \end{aligned}$$

$$\tag{8}$$

The guessing method can be generalized for any arbitrary nature of coupling between different degrees of freedom of system and reservoir – denoted by  $h_1(\upsilon)$  and  $h_2(\chi)$ , through (9):<sup>8,45,46</sup>

$$\begin{split} \dot{r}_{i} &= \frac{p_{i}}{m} - h_{1}(\upsilon) C(r_{i}, p_{i}), \\ \dot{p}_{i} &= F_{i} - h_{2}(\chi) D(r_{i}, p_{i}), \\ \dot{\chi} &= \frac{1}{Q_{\chi}} \left[ \sum_{i=1}^{N} \frac{p_{i}}{m} D(r_{i}, p_{i}) - k_{B} T \frac{\partial D(r_{i}, p_{i})}{\partial p_{i}} \right], \end{split}$$
(9)  
$$\dot{\upsilon} &= \frac{1}{Q_{\upsilon}} \left[ \sum_{i=1}^{N} \frac{\partial U}{\partial r_{i}} C(r_{i}, p_{i}) - k_{B} T \frac{\partial C(r_{i}, p_{i})}{\partial p_{i}} \right]. \end{split}$$

Here  $A(r_i, p_i)$ ,  $B(r_i, p_i)$ ,  $C(r_i, p_i)$ , and  $D(r_i, p_i)$  are arbitrary phase functions, while  $Q_j$ s are constants generally considered to be the masses associated with the heat reservoir. NH equations can be obtained from (9) by setting  $g_{\chi} = \frac{\eta^2}{2}$ ,  $h_2(\chi) = \eta$ ,  $D(r_i, p_i) = p_i$ , and other functions as zero. BT equations can be obtained by setting  $g_{\nu} = \frac{\xi^2}{2}$ ,  $h_2(\nu) = \xi$ ,  $C(r_i, p_i) = \frac{\partial \phi}{\partial r_i}$ and setting all other functions as zero.

# **III. THE PROPOSED THERMOSTAT**

In developing our thermostat, we start with our system being under the influence of two independent heat reservoirs maintained at the same temperature – one influencing the configurational degrees and other influencing the kinetic degrees of freedom. The two independent reservoirs are described, respectively, by the dofs  $\xi$  and  $\eta$ . We propose the following EOM for the extended system and look for the time evolution of  $\dot{\xi}$ ,  $\dot{\eta}$  that generates a canonical distribution:

$$\dot{r}_{i} = \frac{p_{i}}{m_{i}} - \xi \frac{\partial \phi}{\partial r_{i}},$$
  

$$\dot{p}_{i} = -\frac{\partial \phi}{\partial r_{i}} - \eta p_{i},$$
  

$$\dot{\xi} = ?,$$
  

$$\dot{\eta} = ?.$$
(10)

Equation (10) is related to (9) through the transformation  $h_2(\chi) = \eta$ ,  $D(r_i, p_i) = p_i$ ,  $h_2(\upsilon) = \xi$ , and  $C(r_i, p_i) = \frac{\partial \phi}{\partial r_i}$ . While the choice may seem arbitrary at this stage, it will be shown that (10) controls both the kinetic and configurational temperatures:  $-\xi \frac{\partial \phi}{\partial r_i}$  constrains velocity by influencing the generalized positions of the particles,<sup>22</sup> while  $-\eta p_i$  constrains force by acting upon the generalized momenta of the particles. These constraints are imposed in such a way that the both the configurational and kinetic temperatures are equal to the desired temperature  $T_0$ . Due to their mutual independence, the variables  $\xi$  and  $\eta$  are, respectively, able to influence the two independent sets of dofs of the system.

Let the extended phase-space density function be denoted by  $\rho(\Gamma, \xi, \eta)$  where  $\Gamma = \{r_i, p_i\}$ . Since  $\Gamma, \xi$ , and  $\eta$  are independent of each other,  $\rho(\Gamma, \xi, \eta)$  is the product of three density functions corresponding to the system,  $\xi$  and  $\eta$ , respectively:

$$\rho\left(\Gamma,\xi,\eta\right) = \rho_{sys}\left(\Gamma\right)f\left(\xi\right)g\left(\eta\right). \tag{11}$$

The EOM of the system and each reservoir should be such that they sample from canonical distribution, in other words:

$$\rho_{sys} (\Gamma) = e^{-\beta H(\Gamma)},$$
  

$$f (\xi) \propto e^{-c_1 \xi^2},$$
  

$$g (\eta) \propto e^{-c_2 \eta^2}.$$
(12)

Therefore,  $\rho(\Gamma, \xi, \eta) = \frac{e^{-\beta H(\Gamma)}e^{-c_1\xi^2}e^{-c_2\eta^2}}{Z}$  where *Z*, *c*<sub>1</sub>, and *c*<sub>2</sub> are constants. Liouville's equation corresponding to the extended system with 6N+2 dimensions is

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \sum_{i=1}^{3N} \left( \dot{r}_i \frac{\partial\rho}{\partial r_i} + \dot{p}_i \frac{\partial\rho}{\partial p_i} \right) + \dot{\xi} \frac{\partial\rho}{\partial\xi} + \dot{\eta} \frac{\partial\rho}{\partial\eta} + \rho \left[ \sum_{i=1}^{3N} \left( \frac{\partial\dot{r}_i}{\partial r_i} + \frac{\partial\dot{p}_i}{\partial p_i} \right) + \frac{\partial\dot{\xi}}{\partial\xi} + \frac{\partial\dot{\eta}}{\partial\eta} \right].$$
(13)

When steady state is reached, Liouville's equation reduces to (14). The problem of determining the unknown parameters  $(\dot{\xi} \text{ and } \dot{\eta})$  is now simplified to finding the stationary solution of (14):

$$\sum_{i=1}^{3N} \left( \dot{r}_i \frac{\partial \rho}{\partial r_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right) + \dot{\xi} \frac{\partial \rho}{\partial \xi} + \dot{\eta} \frac{\partial \rho}{\partial \eta} + \rho \left[ \sum_{i=1}^{3N} \left( \frac{\partial \dot{r}_i}{\partial r_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) + \frac{\partial \dot{\xi}}{\partial \xi} + \frac{\partial \dot{\eta}}{\partial \eta} \right] = 0. \quad (14)$$

One can treat the terms  $\xi$  and  $\eta$  of the extended system as generalized velocity associated with the corresponding reservoirs. As a result, it is reasonable to assume that they are independent of their respective time derivatives, i.e.,  $\frac{\partial \xi}{\partial \xi} = \frac{\partial \eta}{\partial \eta} = 0$ . From (1) and (10), the remaining terms of (14) can be written as

$$\frac{\partial \rho}{\partial r_i} = -\beta \rho \frac{\partial \phi}{\partial r_i}; \frac{\partial \rho}{\partial p_i} = -\beta \rho \frac{p_i}{m_i}; \frac{\partial \rho}{\partial \xi} = \rho \frac{\partial (\log f)}{\partial \xi},$$

$$\frac{\partial \rho}{\partial \eta} = \rho \frac{\partial (\log g)}{\partial \eta}; \frac{\partial \dot{r}_i}{\partial r_i} = -\xi \frac{\partial^2 \phi}{\partial r_i^2}; \frac{\partial \dot{p}_i}{\partial p_i} = -\eta.$$
(15)

Substituting everything into (14) yields

$$\dot{\xi} \frac{\partial (\log f)}{\partial \xi} + \xi \beta \sum_{i=1}^{3N} \left( \left( \frac{\partial \phi}{\partial r_i} \right)^2 - k_B T_0 \frac{\partial^2 \phi}{\partial r_i^2} \right)$$
$$= -\left[ \dot{\eta} \frac{\partial (\log g)}{\partial \eta} + \eta \beta \sum_{i=1}^{3N} \left( \frac{p_i^2}{m_i} - k_B T_0 \right) \right]. \quad (16)$$

The LHS of (16) is just a function of  $\xi$ ,  $\dot{\xi}$ , while the RHS is just a function of  $\eta$ ,  $\dot{\eta}$ . Thus, each must be equal to some constant *k*. The appropriate value of *k* can be found by considering the long-term evolution of either  $\xi$  (or  $\eta$ ). In steady state,  $\xi$  must fluctuate around a mean value in such a way that the configurational temperature is constrained to the desired value. This can only happen if the long time average of  $\dot{\xi}$ tends to zero. The long-term average of the LHS of (16) gives

$$\left\langle \dot{\xi} \frac{\partial(\log f)}{\partial \xi} \right\rangle + \left\langle \xi \beta \sum_{i=1}^{3N} \left( \left( \frac{\partial \phi}{\partial r_i} \right)^2 - k_B T_0 \frac{\partial^2 \phi}{\partial r_i^2} \right) \right\rangle = k.$$
(17)

Using the independence of  $\dot{\xi}$  with  $\xi$  and  $\xi$  with  $(r_i, p_i)$ , (17) can be rearranged to

$$k = \beta \langle \xi \rangle \left\langle \left[ \left[ \frac{\sum_{i=1}^{3N} \left( \frac{\partial \phi}{\partial r_i} \right)^2}{\sum_{i=1}^{3N} \left( \frac{\partial^2 \phi}{\partial r_i^2} \right)} - k_B T_0 \right] \left[ \sum_{i=1}^{3N} \left( \frac{\partial^2 \phi}{\partial r_i^2} \right) \right] \right\rangle$$
$$= \beta \langle \xi \rangle \left\langle [k_B T_{config} - k_B T_0] \left[ \sum_{i=1}^{3N} \left( \frac{\partial^2 \phi}{\partial r_i^2} \right) \right] \right\rangle.$$
(18)

From (6),  $T_0$  is equal to  $T_{Rugh} = T_{config}$ . Therefore, k is equal to zero. The time evolution of  $\xi$  is thus given by

$$\dot{\xi} = -\frac{\xi\beta}{\partial\left(\log f\right)/\partial\xi} \sum_{i=1}^{3N} \left( \left(\frac{\partial\phi}{\partial r_i}\right)^2 - k_B T \frac{\partial^2\phi}{\partial r_i^2} \right).$$
(19)

Since we have assumed that  $\dot{\xi}$  is just a function of only the particles positions and momenta  $-\frac{\xi\beta}{\partial(\log f)/\partial\xi}$  must be a constant  $(Q_{\xi})$ .

Using similar arguments, the temporal evolution of  $\eta$  can be expressed as

$$\dot{\eta} = \frac{1}{Q_{\eta}} \sum_{i=1}^{3N} \left( \frac{p_i^2}{m_i} - k_B T_0 \right),$$
(20)

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where  $Q_{\eta} = \frac{-\eta\beta N}{\partial(\log g)/\partial \eta}$ . The final EOM of our thermostat are

$$\begin{split} \dot{r}_{i} &= \frac{p_{i}}{m_{i}} - \xi \frac{\partial \phi}{\partial r_{i}}, \\ \dot{p}_{i} &= -\frac{\partial \phi}{\partial r_{i}} - \eta p_{i}, \\ \dot{\xi} &= \frac{1}{Q_{\xi}} \sum_{i=1}^{3N} \left( \left( \frac{\partial \phi}{\partial r_{i}} \right)^{2} - k_{B} T_{0} \frac{\partial^{2} \phi}{\partial r_{i}^{2}} \right), \\ \dot{\eta} &= \frac{1}{Q_{\eta}} \sum_{i=1}^{3N} \left( \frac{p_{i}^{2}}{m_{i}} - k_{B} T_{0} \right). \end{split}$$

$$(21)$$

Thus, the temperature of the system is fixed by making the time derivatives of the feedback variables dependent on the instantaneous difference between the desired temperature and the instantaneous temperature corresponding to feedback variable. The mean-squared feedback (MSF) of the proposed thermostat is decomposed into two parts:

$$MSF_{\eta} = \left\langle \eta^2 \sum_{i=1}^{N} p_i^2 \right\rangle$$
 and  $MSF_{\xi} = \left\langle \xi^2 \sum_{i=1}^{N} F_i^2 \right\rangle$ . (22)

Similarly, from (7) and (8),  $MSF_{NH} = \langle \eta^2 \sum_{i=1}^{N} p_i^2 \rangle$  and  $MSF_{BT} = \langle \xi^2 \sum_{i=1}^{N} F_i^2 \rangle$ . At this point we highlight that just like the original NH and BT formulations, the rate of convergence of the proposed thermostat to canonical ensemble is dependent on the choice of thermostat mass factors.<sup>47,48</sup> Since, the appropriate value of mass parameter is dependent on system properties, a unified principle for its selection is difficult to determine.

The proposed EOM satisfy the extended Liouville's equation even if the coupling terms are augmented with a switching function in such a manner that only a small subdomain is thermostatted. As has been recently shown in the context of NH dynamics,<sup>49</sup> this kind of a partial thermostatting also generates a canonical distribution. The utility of partial thermostatting is manifold – especially for situations, which demand different regions to be thermostatted at different temperatures.

Under the given nature of coupling, (21) is the only solution that simultaneously satisfies Liouville's equation and generates a canonical distribution, i.e., the solution is unique. The proposed EOM satisfy (9). However, if the coefficients are chosen per the criteria spelled out in (9) without going through Eqs. (16)–(20), it would not have been possible to justify why the EOM controlled both the kinetic and configurational temperatures. We now perform simulations to check the performance of our thermostatting scheme.

# **IV. SIMULATION RESULTS**

We subject a system comprising of 2000 atoms to three different studies – equilibrium, sudden temperature change, and steady state thermal conduction, under three different thermostats – the proposed one, Nose-Hoover, and Braga-Travis, and compare the performance of the three. The sys-



FIG. 1. Thermostatting scheme: Full thermostatting (left) and partial thermostatting (right).

tem domain is a cubic box having an edge length of L = 14A with periodic boundary conditions in all the directions. Initial particle positions are sampled from a uniform distribution and their velocities from the Maxwell-Boltzmann distribution. Pair wise interaction ( $\phi_{ij}$ ) of Lennard-Jones type with a cut-off radius of 2.5 is assumed:

$$\phi_{ij} = \begin{cases} 4 \left[ \left( \frac{1}{r_{ij}} \right)^{12} - \left( \frac{1}{r_{ij}} \right)^{6} \right] & r_{ij} \le 2.5 \\ 0 & r_{ij} > 2.5 \end{cases}$$
(23)

Equilibration is achieved in two steps: first a conjugate gradient-based energy minimization followed by 50 000 MD steps. The integration in MD is performed using the Gear Predictor-Corrector algorithm<sup>50</sup> for the proposed and NH thermostats, and the Velocity-Verlet algorithm for BT thermostat, the time step being 0.001 fs for both. We compute three temperatures in each study –  $T_{kinetic}$  using (2),  $T_{config}$  using (3), and  $T_{Rugh}$  using (5).

We thermostat the entire domain in the first example (i.e., equilibrium study) as shown in Fig. 1 (left). For the second example (i.e., temperature change) we look at both: thermostatting the entire domain as before, and partial thermostatting in which only 20% of the domain is thermostatted as shown in Fig. 1 (right) with  $T_{LEN} = 0.10$  L. This kind of arrangement ensures that periodic boundary conditions can be implemented without breaking symmetry and can be used to thermostat two regions at two different temperatures.

The proposed EOM for the entire domain are generalized as

$$\begin{split} \dot{r}_{i} &= \frac{p_{i}}{m_{i}} - \xi \frac{\partial \phi}{\partial r_{i}} S(r_{i}), \\ \dot{p}_{i} &= -\frac{\partial \phi}{\partial r_{i}} - \eta p_{i} S(r_{i}), \\ \dot{\xi} &= \frac{1}{Q_{\xi}} \sum_{i=1}^{3N} \left( \left( \frac{\partial \phi}{\partial r_{i}} \right)^{2} - k_{B} T_{0} \frac{\partial^{2} \phi}{\partial r_{i}^{2}} \right) S(r_{i}), \\ \dot{\eta} &= \frac{1}{Q_{\eta}} \sum_{i=1}^{3N} \left( \frac{p_{i}^{2}}{m_{i}} - k_{B} T_{0} \right) S(r_{i}). \end{split}$$

$$(24)$$

The switch  $S(r_i)$  is an indicator function taking up a value of 1 when the *i*th particle is in the thermostatted region. The NH and BT EOM are generalized similarly. In the third example (i.e., thermal conduction), the regions 1 and 2 in Fig. 1 (right) are thermostatted at two different temperatures.

The fluctuations in steady-state temperature are sensitive to the masses of the thermostat: if the value is too small,

TABLE I. Mass factors and mean-squared feedback of different thermostats for full thermostatting.

Thermostat	Mass factor	MSF
NH	$2.5 \times 10^{3}$	11.530
BT	$1.0 \times 10^{8}$	0.074
Proposed	$Q_{\eta} = 7.5 \times 10^3$	18.825
	$Q_{\xi} = 1.0 \times 10^8$	0.014
	For partial thermostatting, the factors are divided by 5	

the temperature can fluctuate rapidly; if it is too large, the temperature will take a very long time to equilibrate. We begin with choosing a mass factor for NH thermostat, and subsequently tune the mass factors of the other two. We account for the slow relaxation of the configurational degrees in comparison to their momentum counterpart<sup>23</sup> by assuming  $MSF_{BT}$ to be approximately two orders smaller than  $MSF_{NH}$ . The mass factors for the proposed thermostat are chosen such that  $MSF_{\eta}$  ( $MSF_{\xi}$ ) is of the same order as that of  $MSF_{NH}(MSF_{BT})$ . Table I lists the mass factors corresponding to full thermostatting; in case of partial thermostatting the factors are divided by 5.

# A. System in thermal equilibrium

This example is designed to compare how well the proposed thermostat controls temperature vis-à-vis the other two. The equilibrated system, with properties as described above, is thermostatted at a reduced temperature of 2. Post equilibration, the system is observed for 450 000 time steps. Fig. 2 shows the time history of the three temperatures (kinetic, configurational, and Rugh's) as controlled by the three respective thermostats. The temperature statistics over these 450 000

TABLE II. Mean (standard deviation) of different temperatures for the thermostats.

Thermostat	Kinetic	Configurational	Rugh's	
Proposed	2.00 (0.06)	2.00 (0.10)	1.99 (0.10)	
NH	2.00 (0.03)	1.99 (0.09)	1.99 (0.09)	
BT	2.01 (0.04)	2.00 (0.10)	2.00 (0.09)	

sample points are given in Table II. Several inferences can be drawn from the results. First, all three thermostats adequately conserve both the kinetic and configurational temperatures, thereby validating (6). Mean temperature obtained through all the thermostats is nearly at the desired value with coefficient of variation being less than 0.5%.

As described before, these fluctuations are sensitive to thermostat mass factors. Nevertheless, the mean temperature would remain the same because the EOM work on the principles of feedback loop; as a result of which the temperature fluctuates around the desired temperature. Second, we can see that instantaneous Rugh's temperature follows configurational temperature much more closely than kinetic temper-

ature. This occurs because of the larger magnitude of 
$$\sum_{i=1}^{N} \nabla_r^2 \phi$$
  
and  $\sum_{i=1}^{N} \|\nabla_r \phi\|^2$  in comparison to  $\sum_{i=1}^{3N} \frac{1}{m_i}$  and  $\sum_{i=1}^{N} (\frac{p_i}{m_i})^2$ .

The CPU time needed by the three thermostats is comparable. Table III shows the CPU time required for controlling the system temperature over 500 000 MD time steps using the three different thermostats. Understandably, NH thermostat is slightly faster than the other two, since the computationally expensive step of calculating spatial gradient of force (required for calculation calculating  $T_{config}$ ) is not needed.



FIG. 2. Temperature time history for system in equilibrium under (a) proposed thermostat, (b) NH thermostat, and (c) BT thermostat.

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TABLE III. CPU time for 500 000 MD time steps using different thermostats.

	Proposed thermostat	NH thermostat	BT thermostat
CPU time (s)	7451	7170	7477

### B. System subjected to sudden temperature changes

We now subject our system to sudden temperature changes: at 500 000 time step the reservoir temperature rises from 2 to 4 and again comes down to 2 at time step 1 000 000. We continue the simulations up to time step 1 500 000. These simulations are intended to judge the relative robustness of the proposed thermostat to those of NH and BT thermostats. We define robustness as the ability of the thermostat to quickly equilibrate the system under sudden temperature changes and measure it in terms of the time,  $t_{eq}$  required by the fluctuations upon introducing a change in temperature to reach a magnitude comparable to long term fluctuations. We believe this definition of robustness is more general than that in Braga and Travis<sup>22</sup> who adopted a similar example for analyzing the robustness of different thermostatting schemes.

Since the temperature time history in this case is nonstationary, we cannot invoke the ergodicity principle. Instead, we compute temperature as the ensemble average (cf. the second expression of (4)) from 5 sample paths each arising from a randomly sampled initial phase point. We consider



FIG. 3. Temperature control by proposed (black), NH (red), and BT (green) thermostats under full thermostatting (left) and partial thermostatting (right).

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TABLE IV. Time steps  $t_{eq}$  needed to equilibrate under sudden temperature changes.

	Full thermostatting		Partial thermostatting		
	1st change	2nd change	1st change	2nd change	
	Kinetic temperature				
Proposed thermostat	1000	80 000	3000	18 000	
NH thermostat	100 000	154 000	30 000	40 000	
BT thermostat	1000	3000	11 000	25 000	
	Configurational temperature				
Proposed thermostat	1000	2000	4000	7000	
NH thermostat	100 000	140 000	22 000	25 000	
BT thermostat	1000	2000	9000	13 000	
	Rugh's temperature				
Proposed thermostat	1000	2000	4000	7000	
NH thermostat	100 000	140 000	22 000	25 000	
BT thermostat	1000	2000	9000	13 000	

two cases – when the entire system is thermostatted and when 20% of the system is thermostatted as described in Fig. 1 (right). Fig. 3 shows how the three thermostats control the three different temperatures under full as well as partial thermostatting. We observe that the initial fluctuations are not symmetric about the mean, and although all thermostats achieve the desired temperature in the end, they are not equally robust.

Table IV lists  $t_{eq}$  for both full and partial thermostatting. All thermostats (in both full as well as partial thermostatting) take significantly longer to bring the system into equilibrium after the second change. Under full thermostatting, BT thermostat equilibrates the system fastest while under partial thermostatting, the proposed thermostat is able to equilibrate the system fastest. The NH thermostat, in comparison, causes large initial fluctuations in the temperatures and takes the longest to equilibrate. Overall, the proposed and BT thermostats perform comparably with NH thermostat performing the worst.

Interestingly, the partial thermostatting scheme is able to equilibrate the system faster than the full thermostatting scheme in all cases. We attribute this to the fact that decrease in thermostatting mass factors is not commensurate with the decreased number of particles getting thermostatted. This again emphasizes the need for careful selection of thermostat mass factors.

#### C. Steady state thermal conduction

Our third example is non-equilibrium steady state thermal conduction. Molecular dynamics based thermal conduction has been used extensively for studying the behavior and properties of several systems.<sup>51-57</sup> Most of these works invoke kinetic temperature based thermostats for temperature control. As we shall see later, NH and BT thermostats are incapable of generating consistent temperature profiles along the conduction length in the presence of LTE. This example is designed to judge the relative consistency of the three thermostats. We define consistency of a thermostat as the difference between the configurational and kinetic temperatures in a region under LTE: the smaller the difference, the more consistent the thermostat is. Through this example, we show that controlling both the kinetic and configurational temperatures using the proposed thermostat results in a more consistent temperature control than either NH or BT thermostats.

For this study, we keep region 2 of Fig. 1 (right) at a higher temperature of 3 and region 1 at a lower temperature of 1. The domain is divided into 10 strips of equal width  $(=T_{LEN})$  along x such that strips 1 and 10 are at temperature 1 and strips 5 and 6 are at the higher temperature 3. Kinetic, configurational, and Rugh's temperatures are evaluated for each strip as temporal averages over 500 000 steps (according to (2), (3), and (5), respectively). The results are plotted in Fig. 4. For symmetry, only half the domain is shown.

When a system is subjected to non-equilibrium conditions like thermal conduction, the three temperatures at a given location (including the thermostatted ends) would be the same (cf. (6)) only under the existence of LTE. For any system to exhibit LTE, the local kinetic temperature (measured in terms of the variance of the velocity distribution) as calculated from the first three even moments must agree with



FIG. 4. Temperature profile along the conduction direction for proposed thermostat (blue), NH thermostat (red), and BT thermostat (green).

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FIG. 5. Existence of Local Thermal Equilibrium (LTE) under different thermostats.

each other:58,59

$$\langle v^2 \rangle_{\text{local}} = \sqrt{\frac{\langle v^4 \rangle_{\text{local}}}{3}} = \sqrt[3]{\frac{\langle v^6 \rangle_{\text{local}}}{15}}.$$
 (25)

Here,  $\langle \rangle_{local}$  indicates average carried over particles in a small region. Equation (25) indicates that local velocity distribution is Gaussian and hence, the region is in LTE. Figure 5 shows the variance of the velocity distribution at each strip of our system when controlled by the three different thermostats. Clearly the three measures of variance are practically indistinguishable, and hence each thermostat is able to ensure LTE for the heat conduction problem. It therefore follows that due to the existence of LTE, the configurational and Rugh's temperatures at a given location must equal the kinetic temperature, which would be the test of consistency of the thermostat.

A close look at Fig. 4 shows that there is a significant difference between configurational and kinetic temperatures across the conduction length for both the BT configurational thermostat and the NH kinetic thermostat. At the cold and hot thermostatted ends (strips 1 and 5, respectively), the relative difference  $|T_{kinetic} - T_{config}|/T_{kinetic}$  is 5% and 20%, respectively, when the system is under NH thermostatting, and 8% and 4%, respectively, under BT thermostatting. The difference under our thermostat is negligible (1% or less) clearly showing that the proposed thermostat, which controls temperature using the entire phase space variables, is more consistent. The same conclusion holds for regions between the thermostatted ends (strips 2, 3, and 4). The relative difference under our thermostat continues to be negligible, while BT outperforms NH substantially. The existence of local thermal equilibrium in the individual strips ensures that temperature of each strip can be measured with an external thermometer. However, a significant difference in the kinetic and configurational temperatures would render the measured temperature meaningless which would be the direct consequence of using a thermostatting scheme that lacks consistency.

## **V. CONCLUSIONS**

In this work a new thermostat has been proposed that controls both the configurational and kinetic degrees of freedom, each set being coupled with an independent reservoir dof. Steady-state Liouville's equation for the canonical phasespace distribution leads to four unique EOM with the useful property that they generate the canonical ensemble if the system is ergodic. The proposed EOM are a subset of more generalized (9).

We subjected a 2000 atom LJ type system to three different studies – equilibrium, sudden temperature change to judge robustness, and steady state thermal conduction to judge consistency, under three different thermostats – the proposed one, Nose-Hoover, and Braga-Travis, and compared the performance of the three.

In the equilibrium scenario the performances of the three thermostats were very similar, as were the CPU times taken by them. In the sudden temperature change problem, NH fared the worst. While BT thermostat was more robust in the full thermostatting case, the proposed thermostat came out better under partial thermostatting. Overall the robustness of the proposed thermostat was about same as that of BT thermostat.

In non-equilibrium scenarios, dynamical properties are temperature and thermostatting scheme dependent. NH (BT) thermostat works by constraining the kinetic (configurational) temperature. The proposed thermostat circumvents this dependence by constraining both the kinetic and configurational temperatures. In our steady-state thermal conduction problem, there was a substantial difference in the configurational and kinetic temperature along the conduction length for NH and BT thermostats even though we established LTE to exist in our system. The proposed thermostat was able to generate relatively the most consistent temperature profile with minimal difference between the configurational and kinetic temperatures. Out of the three thermostats, NH thermostat performs the worst. It is suggested that every thermostat should be subjected to this kind of thermal conduction problem to gauge its efficacy.

Existence of LTE poses another formidable question when a non-equilibrium system is thermostatted using NH and BT thermostats – which temperature is getting measured by the thermometer given the huge difference between kinetic and configurational temperatures. The proposed thermostat renders this question moot since the three temperatures under its control are indistinguishable at any given location. The ergodic characteristics of the proposed thermostat can be improved by addition of stochastic terms. On similar lines a barostat can also be developed.

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