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Bulgac-Kusnezov-Nosé-Hoover thermostats

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In this paper, we formulate Bulgac-Kusnezov constant temperature dynamics in phase space by means of non-Hamiltonian brackets. Two generalized versions of the dynamics are similarly defined, one where the Bulgac-Kusnezov demons are globally controlled by means of a single additional Nosé variable, and another where each demon is coupled to an independent Nosé-Hoover thermostat. Numerically stable and efficient measure-preserving time-reversible algorithms are derived in a systematic way for each case. The chaotic properties of the different phase space flows are numerically illustrated through the paradigmatic example of the one-dimensional harmonic oscillator. It is found that, while the simple Bulgac-Kusnezov thermostat is apparently not ergodic, both of the Nosé-Hoover controlled dynamics sample the canonical distribution correctly.

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I. INTRODUCTION

In condensed matter studies, there are many situations in which molecular dynamics simulation at constant temperature [1–3] is needed. For example, this occurs when magnetic systems are modeled in terms of classical spins [4–7]. Deterministic methods [8–10], based on non-Hamiltonian dynamics [11–19], can sample the canonical distribution provided that the motion in the phase space of the relevant degrees of freedom is ergodic [1,3]. However, classical spin systems are usually formulated in terms of noncanonical variables [20,21], without a kinetic energy expressed through momenta in phase space, so that Nosé dynamics cannot be applied directly. To tackle this problem, Bulgac and Kusnezov (BK) introduced a deterministic constant-temperature dynamics [22–24], which can be applied to spins. A number of numerical approaches to integration of spin dynamics can be found in the literature [25–28]. However, BK dynamics, as any other deterministic canonical phase space flow, is able to correctly sample the canonical distribution *only* if the motion in phase space is ergodic on the timescale of the simulation. In general, this condition is very difficult to check for statistical systems with many degrees of freedom, while it is known that, despite its simplicity, the one-dimensional harmonic oscillator provides a difficult and important challenge for deterministic thermostatting methods [9,29–31].

In this paper, we accomplish two goals. First, by reformulating BK dynamics through non-Hamiltonian brackets [14,15] in phase space, we introduce two generalized versions of the BK time evolution which are able to sample the canonical distribution for a stiff harmonic system. Second, using a recently introduced approach based on the geometry of non-Hamiltonian phase space [19], we are able to derive stable and efficient measure-preserving and time-reversible algorithms in a systematic way for all the phase space flows treated here.

The BK phase space flow introduces temperature control by means of fictitious coordinates (and their associated momenta in an extended phase space) traditionally called "demons." Our generalizations of the BK dynamics are obtained by controlling the BK demons themselves by means of additional Nosé-type variables [8]. In one case, the BK demons are controlled globally by means of a single additional Nosé-Hoover thermostat [8,9]. In the following this will be referred to as Bulgac-Kusnezov-Nosé-Hoover (BKNH) dynamics. In the second case, each demon is coupled to an independent Nosé-Hoover thermostat. This will be called the Bulgac-Kusnezov-Nosé-Hoover chain (BKNHC), and corresponds to "massive" NH thermostatting of the demon variables [32]. The ability to derive numerically stable measure-preserving time-reversible algorithms [19] for Nosé controlled BK dynamics is very encouraging for future applications to thermostatted spin systems.

This paper is organized as follows. In Sec. II, we briefly sketch the unified formalism for non-Hamiltonian phase space flows and measure-preserving integration. The BK dynamics is formulated in phase space and a measure-preserving integration algorithm is derived in Sec. III. The BKNH and BKNH-chain thermostats are treated in Secs. IV and V, respectively. Numerical results for the one-dimensional harmonic oscillator using these thermostats are presented and discussed in Sec. VI. Section VII reports our conclusions.

In addition we include several appendices. A useful operator formula is derived in Appendix A, while invariant measures for the BK, BKNH, and BKNHC phase space flows are derived in Appendices B–D, respectively.

II. NON-HAMILTONIAN BRACKETS AND MEASURE-PRESERVING ALGORITHMS

Consider an arbitrary system admitting a time-independent (extended) Hamiltonian expressed in terms of the phase space coordinates x_i, $i=1,\ldots,2N$. In this case, the Hamiltonian can be interpreted as the conserved energy of the system.

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Upon introducing an antisymmetric tensor field (generalized Poisson tensor [21,33]) in phase space, $\mathcal{B}(\boldsymbol{x})=-\mathcal{B}^T(\boldsymbol{x})$, one can define non-Hamiltonian brackets [14–16] as

$$\{a,b\} = \sum_{i,j=1}^{2n} \frac{\partial a}{\partial x_i}\mathcal{B}_{ij}\frac{\partial b}{\partial x_j}, \tag{1}$$

where $a=a(\boldsymbol{x})$ and $b=b(\boldsymbol{x})$ are two arbitrary phase space functions. The bracket defined in Eq. (1) is classified as non-Hamiltonian [14–16] since, in general, it does not obey the Jacobi relation, i.e., in general the Jacobiator $\mathcal{J}\neq 0$, where [21]

$$\mathcal{J} = \{a,\{b,c\}\} + \{b,\{c,a\}\} + \{c,\{a,b\}\}, \tag{2}$$

with $c=c(\boldsymbol{x})$ arbitrary phase space function (in addition to the functions a and b, previously introduced). If $\mathcal{J}\neq 0$, the tensor $\mathcal{B}_{ij}$ is said to define an "almost-Poisson" structure [34] (such systems have also been called "pseudo-Hamiltonian" [33]).

An energy conserving and in general non-Hamiltonian phase space flow is then defined by the vector field

$$\dot{x}_i = \{x_i,H\} = \sum_{j=1}^{2N} \mathcal{B}_{ij}\frac{\partial H}{\partial x_j}, \tag{3}$$

where conservation of $H(\boldsymbol{x})$ follows directly from the antisymmetry of $\mathcal{B}_{ij}$.

It has previously been shown how equilibrium statistical mechanics can be comprehensively formulated within this framework [16]. It is also possible to recast the above formalism and the corresponding statistical mechanics in the language of differential forms [17,18]. If the matrix $\mathcal{B}$ is invertible (this is true for all the cases considered here), with inverse Ω_{ij}, we can define the 2-form [35]

$$\Omega = \frac{1}{2}\Omega_{ij}dx^i \wedge dx^j. \tag{4}$$

The dynamics of Eq. (3) is then Hamiltonian if and only if the form Eq. (4) is *closed*, i.e., has zero exterior derivative, $d\Omega=0$ [35]. This condition is independent of the particular system of coordinates used to describe the dynamics.

The structure of Eq. (3) can be taken as the starting point for derivation of efficient time-reversible integration algorithms that also preserve the appropriate measure in phase space [19]. Measure-preserving algorithms can be derived upon introducing a splitting of the Hamiltonian

$$H = \sum_{\alpha=1}^{n_s} H_\alpha, \tag{5}$$

which in turn induces a splitting of the Liouville operator associated with the non-Hamiltonian bracket in Eq. (1),

$$L_\alpha x_i = \{x_i,H_\alpha\} = \sum_{j=1}^{2N} \mathcal{B}_{ij}\frac{\partial H_\alpha}{\partial x_j}. \tag{6}$$

When the phase space flow has a nonzero compressibility

$$\kappa = \sum_{i,j=1}^{2N} \frac{\partial \mathcal{B}_{ij}}{\partial x_i}\frac{\partial H}{\partial x_j}, \tag{7}$$

the statistical mechanics must be formulated in terms of a modified phase space measure [12–18]

$$\bar{\omega} = e^{-w(x)}\omega \tag{8}$$

where

$$\omega = dx^1 \wedge dx^2 \wedge \dots \wedge dx^{2N} \tag{9}$$

is the standard phase space volume element (volume form [35]) and the statistical weight $w(x)$ is defined by

$$\frac{dw}{dt} = \kappa(x). \tag{10}$$

It has been shown that, provided the condition

$$\frac{\partial}{\partial x_j}[e^{-w(x)}\mathcal{B}_{ij}] = 0, \quad i=1,\dots 2N \tag{11}$$

is satisfied, then

$$L_\alpha \bar{\omega} = 0 \quad \text{for every} \quad \alpha, \tag{12}$$

so that the volume element $\bar{\omega}$ is invariant under each of the L_α [19]. The condition (11) is satisfied for all the cases considered below, so that, exploiting the decomposition in Eq. (6), algorithms derived by means of a symmetric Trotter factorization of the Liouville propagator:

$$\exp[\tau L] = \prod_{\alpha=1}^{n_s-1} \exp\left[\frac{\tau}{2}L_\alpha\right] \exp \exp[\tau L_{n_x}] \prod_{\beta=1}^{n_s-1} \exp\left[\frac{\tau}{2}L_{n_s-\beta}\right] \tag{13}$$

are not only time-reversible but also measure preserving.

III. PHASE SPACE FORMULATION OF THE BK THERMOSTAT

A phase space formulation of the BK thermostat can be achieved upon introducing the Hamiltonian

$$H^{\mathrm{BK}} = \frac{p^2}{2m} + V(q) + \frac{K_1(p_\zeta)}{m_\zeta} + \frac{K_2(p_\xi)}{m_\xi} + k_BT(\zeta+\xi) \tag{14a}$$

$$= H(q,p) + \frac{K_1(p_\zeta)}{m_\zeta} + \frac{K_2(p_\xi)}{m_\xi} + k_BT(\zeta+\xi), \tag{14b}$$

where (q,p) are the physical degrees of freedom (coordinates and momenta), with mass m, to be simulated at constant temperature T, while ζ and ξ are the BK 'demons', with corresponding inertial parameters m_ζ and m_ξ, and associated momenta (p_ζ,p_ξ) [22–24]. K_1 and K_2 provide the kinetic energy of demon variables, and for the moment are left arbitrary.

Upon defining the phase space point as $x=(q,\zeta,\xi,p,p_\zeta,p_\xi)=(x_1,x_2,x_3,x_4,x_5,x_6)$, one can introduce an antisymmetric BK tensor field as

$$\mathcal{B}^{\mathrm{BK}} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & -G_2 \\ 0 & 0 & 0 & 0 & \frac{\partial G_1}{\partial p} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{\partial G_2}{\partial q} \\ -1 & 0 & 0 & 0 & -G_1 & 0 \\ 0 & -\frac{\partial G_1}{\partial p} & 0 & G_1 & 0 & 0 \\ G_2 & 0 & -\frac{\partial G_2}{\partial q} & 0 & 0 & 0 \end{bmatrix}, \quad (15)$$

where G_1 and G_2 are functions of system variables (p,q) only.

Substituting $\mathcal{B}^{\mathrm{BK}}$ and H^{BK} into Eq. (3), we obtain the energy-conserving equations

$$\dot{q} = \frac{\partial H}{\partial p} - \frac{G_2(q,p)}{m_\xi}\frac{\partial K_2}{\partial p_\xi}, \quad (16a)$$

$$\dot{\zeta} = \frac{1}{m_\zeta}\frac{\partial G_1}{\partial p}\frac{\partial K_1}{\partial p_\zeta}, \quad (16b)$$

$$\dot{\xi} = \frac{1}{m_\xi}\frac{\partial G_2}{\partial q}\frac{\partial K_2}{\partial p_\xi}, \quad (16c)$$

$$\dot{p} = -\frac{\partial H}{\partial q} - \frac{G_1(q,p)}{m_\zeta}\frac{\partial K_1}{\partial p_\zeta}, \quad (16d)$$

$$\dot{p}_\zeta = G_1\frac{\partial H}{\partial p} - k_B T\frac{\partial G_1}{\partial p}, \quad (16e)$$

$$\dot{p}_\xi = G_2\frac{\partial H}{\partial q} - k_B T\frac{\partial G_2}{\partial q}. \quad (16f)$$

The associated invariant measure for the BK flow is discussed in Appendix B.

Algorithm for BK dynamics

In order to derive a measure preserving algorithms, the first step, following Eq. (5), is to introduce a splitting of H^{BK}:

$$H_1^{\mathrm{BK}} = V(q), \quad (17a)$$

$$H_2^{\mathrm{BK}} = \frac{p^2}{2m}, \quad (17b)$$

$$H_3^{\mathrm{BK}} = k_B T\zeta, \quad (17c)$$

$$H_4^{\mathrm{BK}} = k_B T\xi, \quad (17d)$$

$$H_5^{\mathrm{BK}} = \frac{K_1(p_\zeta)}{m_\zeta}, \quad (17e)$$

$$H_6^{\mathrm{BK}} = \frac{K_2(p_\xi)}{m_\xi}. \quad (17f)$$

A measure-preserving splitting of the Liouville operator then follows from Eq. (6):

$$L_1^{\mathrm{BK}} = -\frac{\partial V}{\partial q}\frac{\partial}{\partial p} + G_2\frac{\partial V}{\partial q}\frac{\partial}{\partial p_\xi}, \quad (18a)$$

$$L_2^{\mathrm{BK}} = \frac{p}{m}\frac{\partial}{\partial q} + G_1\frac{p}{m}\frac{\partial}{\partial p_\zeta}, \quad (18b)$$

$$L_3^{\mathrm{BK}} = -k_B T\frac{\partial G_1}{\partial p}\frac{\partial}{\partial p_\zeta}, \quad (18c)$$

$$L_4^{\mathrm{BK}} = -k_B T\frac{\partial G_2}{\partial q}\frac{\partial}{\partial p_\xi}, \quad (18d)$$

$$L_5^{\mathrm{BK}} = \frac{1}{m_\zeta}\frac{\partial G_1}{\partial p}\frac{\partial K_1}{\partial p_\zeta}\frac{\partial}{\partial \zeta} - \frac{G_1}{m_\zeta}\frac{\partial K_1}{\partial p_\zeta}\frac{\partial}{\partial p}, \quad (18e)$$

$$L_6^{\mathrm{BK}} = -\frac{G_2}{m_\xi}\frac{\partial K_2}{\partial p_\xi}\frac{\partial}{\partial q} + \frac{1}{m_\xi}\frac{\partial G_2}{\partial q}\frac{\partial K_2}{\partial p_\xi}\frac{\partial}{\partial \xi}. \quad (18f)$$

Upon choosing a symmetric Trotter factorization of the BK Liouville operator based on the decomposition

$$L^{\mathrm{BK}} = \sum_{\alpha=1}^{8} L_\alpha^{\mathrm{BK}} \quad (19)$$

a measure-preserving algorithm can be produced in full generality.

In practice, a choice of K_1, K_2, G_1, and G_2 must be made in order obtain explicit formulas. In this paper, we make the following simple choices:

$$G_1 = p, \quad (20a)$$

$$G_2 = q, \quad (20b)$$

$$K_1 = \frac{p_\zeta^2}{2}, \quad (20c)$$

$$K_2 = \frac{p_\xi^2}{2}. \quad (20d)$$

In terms of Eqs. (20a)–(20d), the antisymmetric BK tensor becomes

$$\tilde{\mathcal{B}}^{\mathrm{BK}} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & -q \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & -p & 0 \\ 0 & -1 & 0 & p & 0 & 0 \\ q & 0 & -1 & 0 & 0 & 0 \end{bmatrix}, \quad (21)$$

and the Hamiltonian reads

$$\tilde{H}^{\mathrm{BK}} = H(q,p) + \frac{p_\zeta^2}{2m_\zeta} + \frac{p_\xi^2}{2m_\xi} + k_B T(\zeta + \xi). \quad (22)$$

The split Liouville operators now simplify as follows:

$$\tilde{L}_1^{\rm BK} = -\frac{\partial V}{\partial q}\frac{\partial}{\partial p} + q\frac{\partial V}{\partial q}\frac{\partial}{\partial p_\xi}, \tag{23a}$$

$$\tilde{L}_2^{\rm BK} = \frac{p}{m}\frac{\partial}{\partial q} + \frac{p^2}{m}\frac{\partial}{\partial p_\zeta}, \tag{23b}$$

$$\tilde{L}_3^{\rm BK} = -k_B T\frac{\partial}{\partial p_\zeta}, \tag{23c}$$

$$\tilde{L}_4^{\rm BK} = -k_B T\frac{\partial}{\partial p_\xi}, \tag{23d}$$

$$\tilde{L}_5^{\rm BK} = \frac{p_\zeta}{m_\zeta}\frac{\partial}{\partial \zeta} - \frac{p_\zeta}{m_\zeta}p\frac{\partial}{\partial p} + \frac{p_\zeta^2}{m_\zeta}\frac{\partial}{\partial p_\eta}, \tag{23e}$$

$$\tilde{L}_6^{\rm BK} = -\frac{p_\xi}{m_\xi}q\frac{\partial}{\partial q} + \frac{p_\xi}{m_\xi}\frac{\partial}{\partial \xi} + \frac{p_\xi^2}{m_\xi}\frac{\partial}{\partial p_\chi}. \tag{23f}$$

For the purposes of defining an efficient integration algorithm, we combine commuting Liouville operators as follows:

$$L_A^{\rm BK} \equiv \tilde{L}_1^{\rm BK} + \tilde{L}_4^{\rm BK} = F(q)\frac{\partial}{\partial p} + F_{p_\xi}\frac{\partial}{\partial p_\xi}, \tag{24a}$$

$$L_B^{\rm BK} \equiv \tilde{L}_2^{\rm BK} + \tilde{L}_3^{\rm BK} = \frac{p}{m}\frac{\partial}{\partial q} + F_{p_\zeta}\frac{\partial}{\partial p_\zeta}, \tag{24b}$$

$$L_C^{\rm BK} \equiv \tilde{L}_5^{\rm BK} + \tilde{L}_6^{\rm BK} = -\frac{p_\zeta}{m_\zeta}p\frac{\partial}{\partial p} - \frac{p_\xi}{m_\xi}q\frac{\partial}{\partial q} + \frac{p_\zeta}{m_\zeta}\frac{\partial}{\partial \zeta} + \frac{p_\xi}{m_\xi}\frac{\partial}{\partial \xi}, \tag{24c}$$

where

$$F(q) = -\partial V/\partial q, \tag{25a}$$

$$F_{p_\xi} = q\frac{\partial V}{\partial q} - k_B T, \tag{25b}$$

$$F_{p_\zeta} = \frac{p^2}{m} - k_B T. \tag{25c}$$

Defining

$$U_\alpha^{\rm BK}(\tau) = \exp[\tau \tilde{L}_\alpha^{\rm BK}], \tag{26}$$

where $\alpha = A, B, C$, one possible reversible measure-preserving integration algorithm for the BK thermostat is then

$$U(\tau)^{\rm BK} = U_B^{\rm BK}\left(\frac{\tau}{4}\right)U_C^{\rm BK}\left(\frac{\tau}{2}\right)U_B^{\rm BK}\left(\frac{\tau}{4}\right)U_A^{\rm BK}(\tau) \times U_B^{\rm BK}\left(\frac{\tau}{4}\right)U_C^{\rm BK}\left(\frac{\tau}{2}\right)U_B^{\rm BK}\left(\frac{\tau}{4}\right). \tag{27}$$

Using the so-called direct translation technique [36] we can expand the above symmetric breakup of the Liouville operator into a pseudocode form, ready to be implemented on the computer:

$$\text{(i)}\quad \left.\begin{array}{lcl} q & \rightarrow & q + \frac{\tau}{4}\frac{p}{m} \\ p_\zeta & \rightarrow & p_\zeta + \frac{\tau}{4}F_{p_\zeta} \end{array}\right\}: U_B^{\rm BK}\left(\frac{\tau}{4}\right),$$

$$\text{(ii)}\quad \left.\begin{array}{lcl} p & \rightarrow & p\exp\left[-\frac{\tau}{2}\frac{p_\zeta}{m_\zeta}\right] \\ q & \rightarrow & q\exp\left[-\frac{\tau}{2}\frac{p_\xi}{m_\xi}\right] \\ \zeta & \rightarrow & \zeta + \frac{\tau}{2}\frac{p_\zeta}{m_\zeta} \\ \xi & \rightarrow & \xi + \frac{\tau}{2}\frac{p_\xi}{m_\xi} \end{array}\right\}: U_C^{\rm BK}\left(\frac{\tau}{2}\right),$$

$$\text{(iii)}\quad \left.\begin{array}{lcl} q & \rightarrow & q + \frac{\tau}{4}\frac{p}{m} \\ p_\zeta & \rightarrow & p_\zeta + \frac{\tau}{4}F_{p_\zeta} \end{array}\right\}: U_B^{\rm BK}\left(\frac{\tau}{4}\right),$$

$$\text{(iv)}\quad \left.\begin{array}{lcl} p & \rightarrow & p + \tau F \\ p_\xi & \rightarrow & p_\xi + \tau F_{p_\xi} \end{array}\right\}: U_A^{\rm BK}(\tau),$$

$$\text{(v)}\quad \left.\begin{array}{lcl} q & \rightarrow & q + \frac{\tau}{4}\frac{p}{m} \\ \eta & \rightarrow & \eta + \frac{\tau}{4}\frac{p_\eta}{m_\eta} \\ p_\zeta & \rightarrow & p_\zeta + \frac{\tau}{4}F_{p_\zeta} \end{array}\right\}: U_B^{\rm BK}\left(\frac{\tau}{4}\right),$$

$$\text{(vi)}\quad \left.\begin{array}{lcl} p & \rightarrow & p\exp\left[-\frac{\tau}{2}\frac{p_\zeta}{m_\zeta}\right] \\ q & \rightarrow & q\exp\left[-\frac{\tau}{2}\frac{p_\xi}{m_\xi}\right] \\ \zeta & \rightarrow & \zeta + \frac{\tau}{2}\frac{p_\zeta}{m_\zeta} \\ \xi & \rightarrow & \xi + \frac{\tau}{2}\frac{p_\xi}{m_\xi} \end{array}\right\}: U_C^{\rm BK}\left(\frac{\tau}{2}\right),$$

$$\text{(vii)}\quad \left.\begin{array}{lcl} q & \rightarrow & q + \frac{\tau}{4}\frac{p}{m} \\ p_\zeta & \rightarrow & p_\zeta + \frac{\tau}{4}F_{p_\zeta} \end{array}\right\}: U_B^{\rm BK}\left(\frac{\tau}{4}\right).$$

IV. BULGAC-KUSNEZOV-NOSÉ-HOOVER DYNAMICS

The BKNH Hamiltonian

$$H^{\mathrm{BKNH}} = H(q,p) + \frac{K_1(p_\zeta)}{m_\zeta} + \frac{K_2(p_\xi)}{m_\xi} + \frac{p_\eta^2}{2m_\eta} + k_BT(\zeta+\xi) + 2k_BT\eta \tag{28}$$

is simply the BK Hamiltonian augmented by the Nosé variables (η, p_η) with mass m_η. With the antisymmetric BKNH tensor

$$\mathcal{B}^{\mathrm{BKNH}} = \begin{bmatrix} 0 & 0 & 0 & 0 & 1 & 0 & -G_2 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{\partial G_1}{\partial p} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\partial G_2}{\partial q} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & 0 & -G_1 & 0 & 0 \\ 0 & -\frac{\partial G_1}{\partial p} & 0 & 0 & G_1 & 0 & 0 & -p_\zeta \\ G_2 & 0 & -\frac{\partial G_2}{\partial q} & 0 & 0 & 0 & 0 & -p_\xi \\ 0 & 0 & 0 & -1 & 0 & p_\zeta & p_\xi & 0 \end{bmatrix}, \tag{29}$$

we obtain from Eq. (3) equations of motion for the phase space variables $x=(q,\zeta,\xi,\eta,p,p_\zeta,p_\xi,p_\eta) = (x_1,x_2,x_3,x_4,x_5,x_6,x_7,x_8)$:

$$\dot{q} = \frac{\partial H}{\partial p} - \frac{G_2(q,p)}{m_\xi}\frac{\partial K_2}{\partial p_\xi}, \tag{30a}$$

$$\dot{\zeta} = \frac{1}{m_\zeta}\frac{\partial G_1}{\partial p}\frac{\partial K_1}{\partial p_\zeta}, \tag{30b}$$

$$\dot{\xi} = \frac{1}{m_\xi}\frac{\partial G_2}{\partial q}\frac{\partial K_2}{\partial p_\xi}, \tag{30c}$$

$$\dot{\eta} = \frac{p_\eta}{m_\eta}, \tag{30d}$$

$$\dot{p} = -\frac{\partial H}{\partial q} - \frac{G_1(q,p)}{m_\zeta}\frac{\partial K_1}{\partial p_\zeta}, \tag{30e}$$

$$\dot{p}_\zeta = G_1\frac{\partial H}{\partial p} - k_BT\frac{\partial G_1}{\partial p} - p_\zeta\frac{p_\eta}{m_\eta}, \tag{30f}$$

$$\dot{p}_\xi = G_2\frac{\partial H}{\partial q} - k_BT\frac{\partial G_2}{\partial q} - p_\xi\frac{p_\eta}{m_\eta}, \tag{30g}$$

$$\dot{p}_\eta = \frac{p_\zeta}{m_\zeta}\frac{\partial K_1}{\partial p_\zeta} + \frac{p_\xi}{m_\xi}\frac{\partial K_2}{\partial p_\xi} - 2k_BT. \tag{30h}$$

Here, a single Nosé variable is coupled to both of the BK demons ζ and ξ. The associated invariant measure is discussed in Appendix C.

Algorithm for BKNH dynamics

The Hamiltonian can be split as

$$H_1^{\mathrm{BKNH}} = V(q), \tag{31a}$$

$$H_2^{\mathrm{BKNH}} = \frac{p^2}{2m}, \tag{31b}$$

$$H_3^{\mathrm{BKNH}} = k_BT\zeta, \tag{31c}$$

$$H_4^{\mathrm{BKNH}} = k_BT\xi, \tag{31d}$$

$$H_5^{\mathrm{BKNH}} = \frac{K_1(p_\zeta)}{m_\zeta}, \tag{31e}$$

$$H_6^{\mathrm{BKNH}} = \frac{K_2(p_\xi)}{m_\xi}, \tag{31f}$$

$$H_7^{\mathrm{BKNH}} = \frac{p_\eta^2}{2m_\eta}, \tag{31g}$$

$$H_8^{\mathrm{BKNH}} = 2k_BT\eta, \tag{31h}$$

The measure-preserving splitting [19] of the Liouville operator

$$L_\alpha = \mathcal{B}_{ij}^{\mathrm{BKNH}}\frac{\partial H_\alpha^{\mathrm{BKNH}}}{\partial x_j}\frac{\partial}{\partial x_i}, \tag{32}$$

yields

$$L_1^{\mathrm{BKNH}} = -\frac{\partial V}{\partial q}\frac{\partial}{\partial p} + G_2\frac{\partial V}{\partial q}\frac{\partial}{\partial p_\xi}, \tag{33a}$$

$$L_2^{\mathrm{BKNH}} = \frac{p}{m}\frac{\partial}{\partial q} + G_1\frac{p}{m}\frac{\partial}{\partial p_\zeta}, \tag{33b}$$

$$L_3^{\mathrm{BKNH}} = -k_BT\frac{\partial G_1}{\partial p}\frac{\partial}{\partial p_\zeta}, \tag{33c}$$

$$L_4^{\mathrm{BKNH}} = -k_BT\frac{\partial G_2}{\partial q}\frac{\partial}{\partial p_\xi}, \tag{33d}$$

$$L_5^{\mathrm{BKNH}} = \frac{1}{m_\zeta}\frac{\partial G_1}{\partial p}\frac{\partial K_1}{\partial p_\zeta}\frac{\partial}{\partial \zeta} - \frac{G_1}{m_\zeta}\frac{\partial K_1}{\partial p_\zeta}\frac{\partial}{\partial p} + \frac{p_\zeta}{m_\zeta}\frac{\partial K_1}{\partial p_\zeta}\frac{\partial}{\partial p_\eta}, \tag{33e}$$

$$L_6^{\mathrm{BKNH}} = -\frac{G_2}{m_\xi}\frac{\partial K_2}{\partial p_\xi}\frac{\partial}{\partial q} + \frac{1}{m_\xi}\frac{\partial G_2}{\partial q}\frac{\partial K_2}{\partial p_\xi}\frac{\partial}{\partial \xi} + \frac{p_\xi}{m_\xi}\frac{\partial K_2}{\partial p_\xi}\frac{\partial}{\partial p_\eta}, \tag{33f}$$

$$L_7^{\mathrm{BKNH}} = \frac{p_\eta}{m_\eta}\frac{\partial}{\partial \eta} - \frac{p_\eta}{m_\eta}p_\zeta\frac{\partial}{\partial p_\zeta} - \frac{p_\eta}{m_\eta}p_\xi\frac{\partial}{\partial p_\xi}, \tag{33g}$$

$$L_8^{\mathrm{BKNH}} = -2k_BT\frac{\partial}{\partial p_\eta}. \tag{33h}$$

At this stage, we leave the general formulation and adopt the particular choice of K_1, K_2, G_1, and G_2 given in Eq. (20). The antisymmetric BKNH tensor becomes

$$\tilde{\mathcal{B}}^{\mathrm{BKNH}} = \begin{bmatrix} 0 & 0 & 0 & 0 & 1 & 0 & -q & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & 0 & -p & 0 & 0 \\ 0 & -1 & 0 & 0 & p & 0 & 0 & -p_\zeta \\ q & 0 & -1 & 0 & 0 & 0 & 0 & -p_\xi \\ 0 & 0 & 0 & -1 & 0 & p_\zeta & p_\xi & 0 \end{bmatrix}, \tag{34}$$

and the Hamiltonian simplifies to

$$\tilde{H}^{\mathrm{BKNH}} = H(q,p) + \frac{p_\zeta^2}{2m_\zeta} + \frac{p_\xi^2}{2m_\xi} + \frac{p_\eta^2}{2m_\eta} + k_B T(\zeta + \xi) + 2_B T\eta. \tag{35}$$

The split Liouville operators are now

$$\tilde{L}_1^{\mathrm{BKNH}} = -\frac{\partial V}{\partial q}\frac{\partial}{\partial p} + q\frac{\partial V}{\partial q}\frac{\partial}{\partial p_\xi}, \tag{36a}$$

$$\tilde{L}_2^{\mathrm{BKNH}} = \frac{p}{m}\frac{\partial}{\partial q} + \frac{p^2}{m}\frac{\partial}{\partial p_\zeta}, \tag{36b}$$

$$\tilde{L}_3^{\mathrm{BKNH}} = -k_B T\frac{\partial}{\partial p_\zeta}, \tag{36c}$$

$$\tilde{L}_4^{\mathrm{BKNH}} = -k_B T\frac{\partial}{\partial p_\xi}, \tag{36d}$$

$$\tilde{L}_5^{\mathrm{BKNH}} = \frac{p_\zeta}{m_\zeta}\frac{\partial}{\partial \zeta} - \frac{p_\zeta}{m_\zeta}p\frac{\partial}{\partial p} + \frac{p_\zeta^2}{m_\zeta}\frac{\partial}{\partial p_\eta}, \tag{36e}$$

$$\tilde{L}_6^{\mathrm{BKNH}} = -\frac{p_\xi}{m_\xi}q\frac{\partial}{\partial q} + \frac{p_\xi}{m_\xi}\frac{\partial}{\partial \xi} + \frac{p_\xi^2}{m_\xi}\frac{\partial}{\partial p_\eta}, \tag{36f}$$

$$\tilde{L}_7^{\mathrm{BKNH}} = \frac{p_\eta}{m_\eta}\frac{\partial}{\partial \eta} - \frac{p_\eta}{m_\eta}p_\zeta\frac{\partial}{\partial p_\zeta} - \frac{p_\eta}{m_\eta}p_\xi\frac{\partial}{\partial p_\xi}, \tag{36g}$$

$$\tilde{L}_8^{\mathrm{BKNH}} = -2k_B T\frac{\partial}{\partial p_\eta}. \tag{36h}$$

For the purposes of defining an efficient integration algorithm, we combine commuting Liouville operators as follows:

$$L_A^{\mathrm{BKNH}} \equiv \tilde{L}_1^{\mathrm{BKNH}} + \tilde{L}_4^{\mathrm{BKNH}} + \tilde{L}_7^{\mathrm{BKNH}} = F(q)\frac{\partial}{\partial p} + \frac{p_\eta}{m_\eta}\frac{\partial}{\partial \eta} - \frac{p_\eta}{m_\eta}p_\zeta\frac{\partial}{\partial p_\zeta} + \left(-\frac{p_\chi}{m_\chi}p_\xi + F_{p_\xi}\right)\frac{\partial}{\partial p_\xi} \tag{37a}$$

$$\tilde{L}_B^{\mathrm{BKNH}} \equiv \tilde{L}_2^{\mathrm{BKNH}} + \tilde{L}_3^{\mathrm{BKNH}} = \frac{p}{m}\frac{\partial}{\partial q} + F_{p_\zeta}\frac{\partial}{\partial p_\zeta} \tag{37b}$$

$$L_C^{\mathrm{BKNH}} \equiv \tilde{L}_5^{\mathrm{BKNH}} + \tilde{L}_6^{\mathrm{BKNH}} + \tilde{L}_8^{\mathrm{BKNH}} = -\frac{p_\zeta}{m_\zeta}p\frac{\partial}{\partial p} - \frac{p_\xi}{m_\xi}q\frac{\partial}{\partial q} + \frac{p_\zeta}{m_\zeta}\frac{\partial}{\partial \zeta} + \frac{p_\xi}{m_\xi}\frac{\partial}{\partial \xi} + F_{p_\eta}\frac{\partial}{p_\eta}, \tag{37c}$$

where

$$F(q) = -\frac{\partial V}{\partial q}, \tag{38a}$$

$$F_{p_\xi} = q\frac{\partial V}{\partial q} - k_B T, \tag{38b}$$

$$F_{p_\zeta} = \frac{p^2}{m} - k_B T, \tag{38c}$$

$$F_{p_\eta} = \frac{p_\zeta^2}{m_\zeta} + \frac{p_\xi^2}{m_\xi} - 2k_B T. \tag{38d}$$

In L_A there appears an operator with the form

$$L_i = \left(-\frac{p_k}{m_k}p_i + F_{p_i}\right)\frac{\partial}{\partial p_i}, \tag{39}$$

where $(k,i)=(\chi,\xi)$ for L_A. The action of the propagator associated with this operator on p_i is derived in Appendix A, and is given by

$$e^{\tau L_i}p_i = p_i e^{-\tau(p_k/m_k)} + \tau F_{p_i} e^{-\tau(p_k/2m_k)}\left(\tau\frac{p_k}{2m_k}\right)^{-1}\sinh\left[\tau\frac{p_k}{2m_k}\right]. \tag{40}$$

The apparently singular function

$$\left(\tau\frac{p_k}{2m_k}\right)^{-1}\sinh\left[\tau\frac{p_k}{2m_k}\right] \tag{41}$$

is in fact well behaved as $p_k \to 0$, and can be expanded in a Maclaurin series to suitably high order [37]. In our implementation we used an eighth order expansion.

The propagators for the BKNH dynamics can now be defined as

$$U_\alpha^{\mathrm{BKNH}}(\tau) = \exp[\tau\tilde{L}_\alpha^{\mathrm{BKNH}}], \tag{42}$$

where $\alpha=A,B,C$. One possible reversible measure-preserving integration algorithm for the BKNH thermostat can then be derived from the following Trotter factorization:

$$U(\tau)^{\mathrm{BKNH}} = U_B^{\mathrm{BKNH}}\left(\frac{\tau}{4}\right)U_C^{\mathrm{BKNH}}\left(\frac{\tau}{2}\right)U_B^{\mathrm{BKNH}}\left(\frac{\tau}{4}\right)U_A^{\mathrm{BKNH}}(\tau) \times U_B^{\mathrm{BKNH}}\left(\frac{\tau}{4}\right)U_C^{\mathrm{BKNH}}\left(\frac{\tau}{2}\right)U_B^{\mathrm{BKNH}}\left(\frac{\tau}{4}\right). \tag{43}$$

The direct translation technique gives the following pseudocode:

$$\text{(i)}\quad \left.\begin{array}{lcl} q & \to & q+\dfrac{\tau}{4}\dfrac{p}{m} \\ p_\zeta & \to & p_\zeta+\dfrac{\tau}{4}F_{p_\zeta} \end{array}\right\}:U_B^{\mathrm{BKNH}}\left(\frac{\tau}{4}\right),$$

$$\text{(ii)}\quad \left.\begin{array}{lcl} p & \to & p\,\exp\left[-\dfrac{\tau}{2}\dfrac{p_\zeta}{m_\zeta}\right] \\ q & \to & q\,\exp\left[-\dfrac{\tau}{2}\dfrac{p_\xi}{m_\xi}\right] \\ \zeta & \to & \zeta+\dfrac{\tau}{2}\dfrac{p_\zeta}{m_\zeta} \\ \xi & \to & \xi+\dfrac{\tau}{2}\dfrac{p_\xi}{m_\xi} \\ p_\eta & \to & p_\eta+\dfrac{\tau}{2}F_{p_\zeta} \end{array}\right\}:U_C^{\mathrm{BKNH}}\left(\frac{\tau}{2}\right),$$

$$\text{(iii)}\quad \left.\begin{array}{lcl} q & \to & q+\dfrac{\tau}{4}\dfrac{p}{m} \\ p_\zeta & \to & p_\zeta+\dfrac{\tau}{4}F_{p_\zeta} \end{array}\right\}:U_B^{\mathrm{BKNH}}\left(\frac{\tau}{4}\right),$$

$$\text{(iv)}\quad \left.\begin{array}{lcl} p & \to & p+\tau F(q) \\ p_\xi & \to & p_\xi+\tau F_{p_\xi} \\ \eta & \to & \eta+\tau\dfrac{p_\eta}{m_\eta} \\ p_\zeta & \to & p_\zeta\,\exp\left[-\tau\dfrac{p_\eta}{m_\eta}\right] \end{array}\right\}:U_A^{\mathrm{BKNH}}(\tau),$$

$$\text{(v)}\quad \left.\begin{array}{lcl} q & \to & q+\dfrac{\tau}{4}\dfrac{p}{m} \\ p_\zeta & \to & p_\zeta+\dfrac{\tau}{4}F_{p_\zeta} \end{array}\right\}:U_B^{\mathrm{BKNH}}\left(\frac{\tau}{4}\right),$$

$$\text{(vi)}\quad \left.\begin{array}{lcl} p & \to & p\,\exp\left[-\dfrac{\tau}{2}\dfrac{p_\zeta}{m_\zeta}\right] \\ q & \to & q\,\exp\left[-\dfrac{\tau}{2}\dfrac{p_\xi}{m_\xi}\right] \\ \zeta & \to & \zeta+\dfrac{\tau}{2}\dfrac{p_\zeta}{m_\zeta} \\ \xi & \to & \xi+\dfrac{\tau}{2}\dfrac{p_\xi}{m_\xi} \\ p_\eta & \to & p_\eta+\dfrac{\tau}{2}F_{p_\eta} \end{array}\right\}:U_C^{\mathrm{BKNH}}\left(\frac{\tau}{2}\right),$$

$$\text{(vii)}\quad \left.\begin{array}{lcl} q & \to & q+\dfrac{\tau}{4}\dfrac{p}{m} \\ p_\zeta & \to & p_\zeta+\dfrac{\tau}{4}F_{p_\zeta} \end{array}\right\}:U_B^{\mathrm{BKNH}}\left(\frac{\tau}{4}\right).$$

V. BULGAC-KUSNEZOV-NOSÉ-HOOVER CHAIN

For simplicity, we explicitly treat only the case, in which the p_ζ and p_ξ demons are each coupled to a standard Nosé-Hoover thermostat (length one). It would be straightforward to couple each of the demons to NH chains [32], and the general case can be easily inferred from what follows. Define the Hamiltonian

$$\begin{aligned} H^{\mathrm{BKNHC}} &= H(q,p)+\frac{K_1(p_\zeta)}{m_\zeta}+\frac{K_2(p_\xi)}{m_\xi}+\frac{p_\eta^2}{2m_\eta}+\frac{p_\chi^2}{2m_\chi} \\ &\quad +k_BT(\zeta+\xi+\eta+\chi). \end{aligned} \tag{44}$$

Upon defining the phase space point $x=(q,\zeta,\xi,\eta,\chi,p,p_\zeta,p_\xi,p_\eta,p_\chi)=(x_1,x_2,x_3,x_4,x_5,x_6,x_7,x_8,x_9,x_{10})$ and the antisymmetric BKNHC tensor

$$\mathcal{B}^{\mathrm{BKNHC}}=\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 1 & 0 & -G_2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \dfrac{\partial G_1}{\partial p} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dfrac{\partial G_2}{\partial q} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & 0 & 0 & -G_1 & 0 & 0 & 0 \\ 0 & -\dfrac{\partial G_1}{\partial p} & 0 & 0 & 0 & G_1 & 0 & 0 & -p_\zeta & 0 \\ G_2 & 0 & -\dfrac{\partial G_2}{\partial q} & 0 & 0 & 0 & 0 & 0 & 0 & -p_\xi \\ 0 & 0 & 0 & -1 & 0 & 0 & p_\zeta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & p_\xi & 0 & 0 \end{bmatrix}, \tag{45}$$

associated non-Hamiltonian equations of motion are

$$\dot{x}_i = \mathcal{B}_{ij}^{\mathrm{BKNHC}} \frac{\partial H^{\mathrm{BKNHC}}}{\partial x_j} \tag{46}$$

with $i=1,\ldots,10$.

Algorithm for BKNHC chain dynamics

Splitting the BKNHC chain Hamiltonian as

$$H_1^{\mathrm{BKNHC}} = V(q), \tag{47a}$$

$$H_2^{\mathrm{BKNHC}} = \frac{p^2}{2m}, \tag{47b}$$

$$H_3^{\mathrm{BKNHC}} = k_B T \zeta, \tag{47c}$$

$$H_4^{\mathrm{BKNHC}} = k_B T \xi, \tag{47d}$$

$$H_5^{\mathrm{BKNHC}} = \frac{K_1(p_\zeta)}{m_\zeta}, \tag{47e}$$

$$H_6^{\mathrm{BKNHC}} = \frac{K_2(p_\xi)}{m_\xi}, \tag{47f}$$

$$H_7^{\mathrm{BKNHC}} = \frac{p_\eta^2}{2m_\eta}, \tag{47g}$$

$$H_8^{\mathrm{BKNHC}} = k_B T \eta, \tag{47h}$$

$$H_9^{\mathrm{BKNHC}} = \frac{p_\chi^2}{2m_\chi}, \tag{47i}$$

$$H_{10}^{\mathrm{BKNHC}} = k_B T \chi, \tag{47j}$$

we obtain the corresponding measure-preserving splitting of the Liouville operator

$$L_\alpha = \mathcal{B}_{ij}^{\mathrm{BKNHC}} \frac{\partial H_\alpha^{\mathrm{BKNHC}}}{\partial x_j} \frac{\partial}{\partial x_i}. \tag{48}$$

At this stage we go directly to Eq. (20). The antisymmetric Nosé-Hoover-Bulgac-Kusnezov tensor becomes

$$\widetilde{\mathcal{B}}^{\mathrm{BKNHC}} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 1 & 0 & -q & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & 0 & 0 & -p & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & p & 0 & 0 & -p_\zeta & 0 \\ q & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & -p_\xi \\ 0 & 0 & 0 & -1 & 0 & 0 & p_\zeta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & p_\xi & 0 & 0 \end{bmatrix}, \tag{49}$$

the Hamiltonian

$$\widetilde{H}^{\mathrm{BKNHC}} = H(q,p) + \frac{p_\zeta^2}{2m_\zeta} + \frac{p_\xi^2}{2m_\xi} + \frac{p_\eta^2}{2m_\eta} + \frac{p_\chi^2}{2m_\chi} + k_B T(\zeta + \xi + \eta + \chi) \tag{50}$$

and associated Liouville operators

$$\widetilde{L}_1^{\mathrm{BKNHC}} = -\frac{\partial V}{\partial q}\frac{\partial}{\partial p} + q\frac{\partial V}{\partial q}\frac{\partial}{\partial p_\xi}, \tag{51a}$$

$$\widetilde{L}_2^{\mathrm{BKNHC}} = \frac{p}{m}\frac{\partial}{\partial q} + \frac{p^2}{m}\frac{\partial}{\partial p_\zeta}, \tag{51b}$$

$$\widetilde{L}_3^{\mathrm{BKNHC}} = -k_B T\frac{\partial}{\partial p_\zeta}, \tag{51c}$$

$$\widetilde{L}_4^{\mathrm{BKNHC}} = -k_B T\frac{\partial}{\partial p_\xi}, \tag{51d}$$

$$\widetilde{L}_5^{\mathrm{BKNHC}} = \frac{p_\zeta}{m_\zeta}\frac{\partial}{\partial \zeta} - \frac{p_\zeta}{m_\zeta}p\frac{\partial}{\partial p} + \frac{p_\zeta^2}{m_\zeta}\frac{\partial}{\partial p_\eta}, \tag{51e}$$

$$\widetilde{L}_6^{\mathrm{BKNHC}} = -\frac{p_\xi}{m_\xi}q\frac{\partial}{\partial q} + \frac{p_\xi}{m_\xi}\frac{\partial}{\partial \xi} + \frac{p_\xi^2}{m_\xi}\frac{\partial}{\partial p_\chi}, \tag{51f}$$

$$\widetilde{L}_7^{\mathrm{BKNHC}} = \frac{p_\eta}{m_\eta}\frac{\partial}{\partial \eta} - \frac{p_\eta}{m_\eta}p_\zeta\frac{\partial}{\partial p_\zeta}, \tag{51g}$$

$$\widetilde{L}_8^{\mathrm{BKNHC}} = -k_B T\frac{\partial}{\partial p_\eta}, \tag{51h}$$

$$\widetilde{L}_9^{\mathrm{BKNHC}} = \frac{p_\chi}{m_\chi}\frac{\partial}{\partial \chi} - \frac{p_\chi}{m_\chi}p_\xi\frac{\partial}{\partial p_\xi}, \tag{51i}$$

$$\widetilde{L}_{10}^{\mathrm{BKNHC}} = -k_B T\frac{\partial}{\partial p_\chi}. \tag{51j}$$

We combine commuting Liouville operators as follows:

$$L_A^{\mathrm{BKNHC}} \equiv \widetilde{L}_1^{\mathrm{BKNHC}} + \widetilde{L}_4^{\mathrm{BKNHC}} + \widetilde{L}_9^{\mathrm{BKNHC}} = F(q)\frac{\partial}{\partial p} + \frac{p_\chi}{m_\chi}\frac{\partial}{\partial \chi} + \left(-\frac{p_\chi}{m_\chi}p_\xi + F_{p_\xi}\right)\frac{\partial}{\partial p_\xi}, \tag{52a}$$

$$L_B^{\mathrm{BKNHC}} \equiv \tilde{L}_2^{\mathrm{BKNHC}} + \tilde{L}_3^{\mathrm{BKNHC}} + \tilde{L}_7^{\mathrm{BKNHC}} = \frac{p}{m}\frac{\partial}{\partial q} + \frac{p_\eta}{m_\eta}\frac{\partial}{\partial \eta} + \left(-\frac{p_\eta}{m_\eta}p_\zeta + F_{p_\zeta}\right)\frac{\partial}{\partial p_\zeta}, \tag{52b}$$

$$L_C^{\mathrm{BKNHC}} \equiv \tilde{L}_5^{\mathrm{BKNHC}} + \tilde{L}_6^{\mathrm{BKNHC}} + \tilde{L}_8^{\mathrm{BKNHC}} + \tilde{L}_{10}^{\mathrm{BKNHC}} = -\frac{p_\zeta}{m_\zeta}p\frac{\partial}{\partial p} - \frac{p_\xi}{m_\xi}q\frac{\partial}{\partial q} + \frac{p_\zeta}{m_\zeta}\frac{\partial}{\partial \zeta} + \frac{p_\xi}{m_\xi}\frac{\partial}{\partial \xi} + F_{p_\eta}\frac{\partial}{p_\eta} + F_{p_\chi}\frac{\partial}{p_\chi}, \tag{52c}$$

where

$$F(q) = -\frac{\partial V}{\partial q}, \tag{53a}$$

$$F_{p_\xi} = q\frac{\partial V}{\partial q} - k_B T, \tag{53b}$$

$$F_{p_\zeta} = \frac{p^2}{m} - k_B T, \tag{53c}$$

$$F_{p_\eta} = \frac{p_\zeta^2}{m_\zeta} - k_B T, \tag{53d}$$

$$F_{p_\chi} = \frac{p_\xi^2}{m_\xi} - k_B T. \tag{53e}$$

Both in L_A^{BKNHC} and L_B^{BKNHC} there appears an operator with the form

$$L_i = \left(-\frac{p_k}{m_k}p_i + F_{p_i}\right)\frac{\partial}{\partial p_i}, \tag{54}$$

where $(k,i)=(\chi,\xi)$ for L_A and $(k,i)=(\eta,\zeta)$ for L_B. Again following the derivation in Appendix A, we find

$$e^{\tau L_i}p_i = p_i e^{-\tau(p_k/m_k)} + \tau F_{p_i} e^{-\tau(p_k/2m_k)}\left(\tau\frac{p_k}{2m_k}\right)^{-1}\sinh\left[\tau\frac{p_k}{2m_k}\right]. \tag{55}$$

The function $(\tau\frac{p_k}{2m_k})^{-1}\sinh[\tau\frac{p_k}{2m_k}]$ is treated through an eighth order expansion [37].

The propagators

$$U_\alpha^{\mathrm{BKNHC}}(\tau) = \exp[\tau\tilde{L}_\alpha^{\mathrm{BKNHC}}], \tag{56}$$

with $\alpha=A,B,C$ can now be introduced. One possible reversible measure-preserving integration algorithm for the BKNHC chain thermostat is then

$$U(\tau)^{\mathrm{BKNHC}} = U_B^{\mathrm{BKNHC}}\left(\frac{\tau}{4}\right)U_C^{\mathrm{BKNHC}}\left(\frac{\tau}{2}\right)U_B^{\mathrm{BKNHC}}\left(\frac{\tau}{4}\right) \times U_A^{\mathrm{BKNHC}}(\tau) \times U_B^{\mathrm{BKNHC}}\left(\frac{\tau}{4}\right)U_C^{\mathrm{BKNHC}}\left(\frac{\tau}{2}\right)U_B^{\mathrm{BKNHC}}\left(\frac{\tau}{4}\right). \tag{57}$$

In pseudocode form, we have the resulting integration algorithm:

$$\text{(i)}\quad \left.\begin{aligned} q &\rightarrow q + \frac{\tau}{4}\frac{p}{m} \\ \eta &\rightarrow \eta + \frac{\tau}{4}\frac{p_\eta}{m_\eta} \\ p_\zeta &\rightarrow p_\zeta e^{-(\tau/4)(p_\eta/m_\eta)} + \frac{\tau}{4}F_{p_\zeta}e^{-(\tau/4)(p_\eta/2m_\eta)}\left(\frac{\tau}{4}\frac{p_\eta}{2m_\eta}\right)^{-1}\sinh\left[\frac{\tau}{4}\frac{p_\eta}{2m_\eta}\right] \end{aligned}\right\} : U_B^{\mathrm{BKNHC}}\left(\frac{\tau}{4}\right),$$

$$\text{(ii)}\quad \left.\begin{aligned} p &\rightarrow p\exp\left[-\frac{\tau}{2}\frac{p_\zeta}{m_\zeta}\right] \\ q &\rightarrow q\exp\left[-\frac{\tau}{2}\frac{p_\xi}{m_\xi}\right] \\ \zeta &\rightarrow \zeta + \frac{\tau}{2}\frac{p_\zeta}{m_\zeta} \\ \xi &\rightarrow \xi + \frac{\tau}{2}\frac{p_\xi}{m_\xi} \\ p_\eta &\rightarrow p_\eta + \frac{\tau}{2}F_{p_\zeta} \\ p_\chi &\rightarrow p_\chi + \frac{\tau}{2}F_{p_\chi} \end{aligned}\right\} : U_C^{\mathrm{BKNHC}}\left(\frac{\tau}{2}\right),$$

$$\text{(iii)}\quad \left.\begin{array}{lcl} q & \to & q+\frac{\tau}{4}\frac{p}{m} \\ \eta & \to & \eta+\frac{\tau}{4}\frac{p_\eta}{m_\eta} \\ p_\zeta & \to & p_\zeta e^{-(\tau/4)(p_\eta/m_\eta)}+\frac{\tau}{4}F_{p_\zeta}e^{-(\tau/4)(p_\eta/2m_\eta)}\left(\frac{\tau}{4}\frac{p_\eta}{2m_\eta}\right)^{-1}\sinh\left[\frac{\tau}{4}\frac{p_\eta}{2m_\eta}\right] \end{array}\right\}:U_B^{\mathrm{BKNHC}}\left(\frac{\tau}{4}\right),$$

$$\text{(iv)}\quad \left.\begin{array}{lcl} p & \to & p+\tau F \\ \chi & \to & \chi+\tau\frac{p_\chi}{m_\chi} \\ p_\xi & \to & p_\xi e^{-\tau(p_\chi/m_\chi)}+\tau F_{p_\xi}e^{-\tau(p_\chi/2m_\chi)}\left(\tau\frac{p_\chi}{2m_\chi}\right)^{-1}\sinh\left[\tau\frac{p_\chi}{2m_\chi}\right] \end{array}\right\}:U_A^{\mathrm{BKNHC}}(\tau),$$

$$\text{(v)}\quad \left.\begin{array}{lcl} q & \to & q+\frac{\tau}{4}\frac{p}{m} \\ \eta & \to & \eta+\frac{\tau}{4}\frac{p_\eta}{m_\eta} \\ p_\zeta & \to & p_\zeta e^{-(\tau/4)(p_\eta/m_\eta)}+\frac{\tau}{4}F_{p_\zeta}e^{-(\tau/4)(p_\eta/2m_\eta)}\left(\frac{\tau}{4}\frac{p_\eta}{2m_\eta}\right)^{-1}\sinh\left[\frac{\tau}{4}\frac{p_\eta}{2m_\eta}\right] \end{array}\right\}:U_B^{\mathrm{BKNHC}}\left(\frac{\tau}{4}\right),$$

$$\text{(vi)}\quad \left.\begin{array}{lcl} p & \to & p\exp\left[-\frac{\tau}{2}\frac{p_\zeta}{m_\zeta}\right] \\ q & \to & q\exp\left[-\frac{\tau}{2}\frac{p_\xi}{m_\xi}\right] \\ \zeta & \to & \zeta+\frac{\tau}{2}\frac{p_\zeta}{m_\zeta} \\ \xi & \to & \xi+\frac{\tau}{2}\frac{p_\xi}{m_\xi} \\ p_\eta & \to & p_\eta+\frac{\tau}{2}F_{p_\eta} \\ p_\chi & \to & p_\chi+\frac{\tau}{2}F_{p_\chi} \end{array}\right\}:U_C^{\mathrm{BKNHC}}\left(\frac{\tau}{2}\right),$$

$$\text{(vii)}\quad \left.\begin{array}{lcl} q & \to & q+\frac{\tau}{4}\frac{p}{m} \\ \eta & \to & \eta+\frac{\tau}{4}\frac{p_\eta}{m_\eta} \\ p_\zeta & \to & p_\zeta e^{-(\tau/4)(p_\eta/m_\eta)}+\frac{\tau}{4}F_{p_\zeta}e^{-(\tau/4)(p_\eta/2m_\eta)}\left(\frac{\tau}{4}\frac{p_\eta}{2m_\eta}\right)^{-1}\sinh\left[\frac{\tau}{4}\frac{p_\eta}{2m_\eta}\right] \end{array}\right\}:U_B^{\mathrm{BKNHC}}\left(\frac{\tau}{4}\right).$$

VI. NUMERICAL RESULTS

In its simplicity, the dynamics of a harmonic mode in one dimension is a paradigmatic example for checking the chaotic (ergodic) properties of constant-temperature phase space flows and the correct sampling of the canonical distribution. It is well known that it is necessary to generalize basic Nosé-Hoover dynamics [1,8,9] to thermostats such as the Nosé-Hoover chain [32,37] in order to produce correct constant-temperature averages for systems such as the harmonic oscillator.

Some time ago, BK dynamics was devised to provide a deterministic thermostat for systems such as classical spins

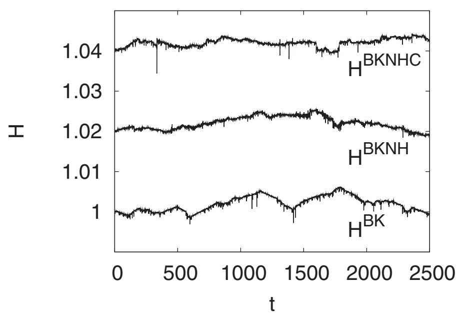

FIG. 1. Comparison of the total extended Hamiltonian versus time (normalized with respect to its value at $t=0$) for the harmonic oscillator undergoing simple Bulgac-Kusnezov dynamics (H^{BK}), NH controlled Bulgac-Kusnezov dynamics (H^{BKNH}), and Bulgac-Kusnezov-Nosé-Hoover chain dynamics (H^{BKNHC}). Two curves have been displaced vertically for clarity. The time-reversible measure-preserving algorithms developed in this paper conserve the extended Hamiltonian to high accuracy in all three cases.

[23,24]. To ensure efficient thermostatting, BK found it necessary to introduce several demons per thermostatted degree of freedom, where each demon was taken to have a different and in principle complicated coupling to the system degree of freedom [23,24]. In the present work, we keep the form of the system-thermostat coupling as simple as possible, in order to facilitate the formulation of explicit, reversible and measure-preserving integrators [19]. It is then of interest to investigate the ability of our BK-type thermostats to produce the correct canonical sampling in the case of the harmonic oscillator. Interest in harmonic modes is also justified by the possibility of devising models of condensed matter systems in terms of coupled spins and harmonic modes, as already done in quantum dynamics with so-called spin-boson models [38]. We therefore investigate the performance of our integration schemes on the simple one-dimensional harmonic oscillator.

For the particular calculations reported here, the oscillator angular frequency, all masses and k_BT were taken to be unity. The time step in all cases was $\tau=0.0025$, and all runs were calculated for 10^6 time steps, starting from the same initial conditions: harmonic oscillator coordinate $q=0.3$, all other phase space variables zero at $t=0$.

The measure-preserving algorithms derived here result in stable numerical integration for all the three cases treated: BK, BKNH, and BKNHC chain dynamics. Figure 1 shows the three extended Hamiltonians (normalized by their respective initial time value) versus time. All three Hamiltonians are *numerically* conserved by the corresponding measure-preserving algorithm to very high accuracy (which is maintained in all the three cases).

However, the basic BK phase space flow is not capable of producing the correct canonical sampling for a harmonic mode. This can be easily checked since the canonical distribution function of the harmonic oscillator is isotropic in phase space and its radial dependence can be calculated exactly. Details of this way of visualizing the phase space sampling have already been given in [14,15]. Figure 2, displaying the comparison between the theoretical and the calculated value of the radial probability in phase space,

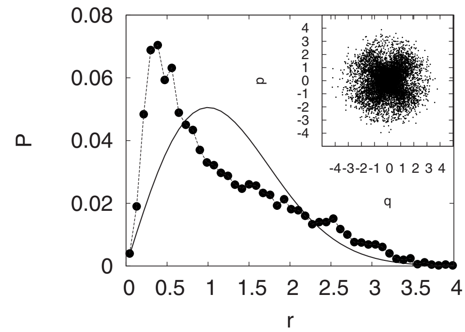

FIG. 2. Radial phase space probability for a harmonic oscillator under Bulgac-Kusnezov dynamics. The continuous line shows the theoretical value while the black bullets display the numerical results. The inset displays a plot of the phase space distribution of points along the single trajectory used to compute the radial probability.

clearly shows that the BK dynamics is not able to produce canonical sampling. A look at the inset of Fig. 2, showing the phase space distribution for the harmonic mode, also immediately shows that the dynamics is not ergodic.

The same analysis has been carried out for BKNH and BKNHC phase space flows, and these are displayed in Figs. 3 and 4, respectively. Within numerical errors, both BKNH and BKNHC thermostats are able to produce the correct canonical distribution for the stiff harmonic modes.

Introduction of a single, global Nosé-type variable in the BKNH thermostat effectively introduces additional coupling between the two demon variables. The effectiveness of the BKNH thermostat is consistent with our findings (results not discussed here) that introduction of explicit coupling between demons in BK thermostat dynamics also leads to efficient thermostatting of the harmonic oscillator.

VII. CONCLUSIONS

We have formulated Bulgac-Kusnezov [23,24], Nosé-Hoover controlled Bulgac-Kusnezov, and Bulgac-Kusnezov-Nosé-Hoover chain thermostats in phase space by means of

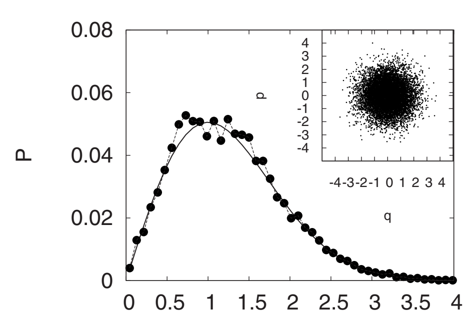

FIG. 3. Radial phase space probability for a harmonic oscillator under Nosé-Hoover controlled Bulgac-Kusnezov dynamics. The continuous line shows the theoretical value while the black bullets display the numerical results. The inset displays a plot of the phase space distribution of points along the single trajectory used to compute the radial probability.

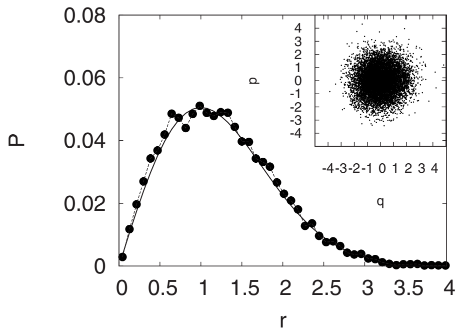

FIG. 4. Radial phase space probability for a harmonic oscillator under Bulgac-Kusnezov-Nosé-Hoover chain dynamics. The continuous line shows the theoretical value while the black bullets display the numerical results. The inset displays a plot of the phase space distribution of points along the single trajectory used to compute the radial probability.

non-Hamiltonian brackets [14,15]. We have derived time-reversible measure-preserving algorithms [19] for these three cases and showed that additional control by a single Nosé-Hoover thermostat or independent Nosé-Hoover thermostats is necessary to produce the correct canonical distribution for a stiff harmonic mode.

Measure-preserving dynamics of the kind discussed here is associated with equilibrium simulations (where, for example, there is a single temperature parameter T). Stationary phase space distributions associated with nonequilibrium situations are much more complicated than the smooth equilibrium densities analyzed in the present paper [11,39,40]. Nonequilibrium simulations of heat flow could be carried out by extending the present approach to multimode systems (e.g., a chain of oscillators) coupled to BK-type demons with associated NH thermostats corresponding to two different temperatures [41–43].

The techniques presented here for derivation and implementation of thermostats have been shown to be efficient and versatile. We anticipate that analogous approaches can be usefully applied to systems of classical spins coupled to both harmonic and anharmonic modes.

APPENDIX A: OPERATOR FORMULA

We wish to determine the action of the propagator associated with the Liouville operator Eq. (39). This is equivalent to solving the evolution equation (recall $i \neq k$)

$$\frac{dp_i}{dt} = \left(-\frac{p_k}{m_k}p_i + F_{p_i}\right), \tag{A1}$$

from $t=0$ to $t=\tau$. Integrating, we have

$$-\frac{m_k}{p_k}\ln\left(-\frac{p_k}{m_k}p_i + F_{p_i}\right)\Bigg|_0^\tau = \tau, \tag{A2}$$

giving

$$p_i(\tau) \equiv \exp\left[\tau\left(-\frac{p_k}{m_k}p_i + F_{p_i}\right)\frac{\partial}{\partial p_i}\right]p_i, \tag{A3a}$$

$$= p_i e^{-\tau p_k/m_k} + \frac{m_k}{p_k}F_{p_i}(1 - e^{-\tau p_k/m_k}), \tag{A3b}$$

$$= p_i e^{-\tau p_k/m_k} + \tau F_{p_i} e^{-\tau p_k/2m_k}\frac{\sinh\left[\tau\dfrac{p_k}{2m_k}\right]}{\tau\dfrac{p_k}{2m_k}}. \tag{A3c}$$

APPENDIX B: INVARIANT MEASURE OF THE BK PHASE SPACE FLOWS

The phase space compressibility of the phase space BK thermostat is

$$\kappa_{\mathrm{BK}} = \frac{\partial \mathcal{B}_{ij}^{\mathrm{BK}}}{\partial x_i}\frac{\partial H_{\mathrm{BK}}}{\partial x_i} = -\frac{1}{m_\zeta}\frac{\partial G_1}{\partial p}\frac{\partial K_1}{\partial p_\zeta} - \frac{1}{m_\xi}\frac{\partial G_2}{\partial q}\frac{\partial K_2}{\partial p_\xi}. \tag{B1}$$

Upon introducing the function

$$H_{\mathrm{T}}^{\mathrm{BK}} = H + \frac{K_1}{m_\zeta} + \frac{K_2}{m_\xi}, \tag{B2}$$

one can easily find that

$$\kappa_{\mathrm{BK}} = \frac{1}{k_B T}\frac{dH_{\mathrm{T}}^{\mathrm{BK}}}{dt}, \tag{B3}$$

so that the invariant measure in phase space reads

$$d\mu = dx \exp\left[-\int_t dt\,\kappa_{\mathrm{BK}}\right], \tag{B4a}$$

$$= dx \exp[-\beta H_{\mathrm{T}}^{\mathrm{BK}}], \tag{B4b}$$

$$= dx \exp[-\beta H^{\mathrm{BK}}]\exp[\zeta + \xi], \tag{B4c}$$

as desired.

APPENDIX C: INVARIANT MEASURE OF THE BKNH PHASE SPACE FLOWS

The phase space compressibility of the NH controlled Bulgac-Kusnezov thermostat is

$$\kappa_{\mathrm{BKNH}} = \frac{\partial \mathcal{B}_{ij}^{\mathrm{BKNH}}}{\partial x_i}\frac{\partial H_{\mathrm{BKNH}}}{\partial x_i}$$

$$= -\frac{1}{m_\zeta}\frac{\partial G_1}{\partial p}\frac{\partial K_1}{\partial p_\zeta} - \frac{1}{m_\xi}\frac{\partial G_2}{\partial q}\frac{\partial K_2}{\partial p_\xi} - 2\frac{p_\eta}{m_\eta}. \tag{C1}$$

Upon introducing the function

$$H_{\mathrm{T}}^{\mathrm{BKNH}} = H + \frac{K_1}{m_\zeta} + \frac{K_2}{m_\xi} + \frac{p_\eta^2}{2m_\eta}, \tag{C2}$$

we have

$$\kappa_{\mathrm{BKNH}} = \frac{1}{k_B T}\frac{dH_{\mathrm{T}}^{\mathrm{BK}}}{dt}, \tag{C3}$$

so that the invariant measure in phase space is

$$d\mu = dx \exp\left[-\int_t dt \kappa_{\mathrm{BKNH}}\right], \tag{C4a}$$

$$= dx \exp[-\beta H_{\mathrm{T}}^{\mathrm{BKNH}}], \tag{C4b}$$

$$= dx \exp[-\beta H^{\mathrm{BKNH}}]\exp[\zeta + \xi + 2\eta]. \tag{C4c}$$

APPENDIX D: INVARIANT MEASURE OF THE BKNHC CHAIN PHASE SPACE FLOWS

The phase space compressibility of the Nosé-Hoover-Bulgac-Kusnezov chain is

$$\kappa_{\mathrm{BKNHC}} = \frac{\partial \mathcal{B}_{ij}^{\mathrm{BKNHC}}}{\partial x_i}\frac{\partial H_{\mathrm{BKNHC}}}{\partial x_i} = -\frac{1}{m_\zeta}\frac{\partial G_1}{\partial p}\frac{\partial K_1}{\partial p_\zeta} - \frac{1}{m_\xi}\frac{\partial G_2}{\partial q}\frac{\partial K_2}{\partial p_\xi} - \frac{p_\eta}{m_\eta} - \frac{p_\chi}{m_\chi}. \tag{D1}$$

Upon introducing the function

$$H_{\mathrm{T}}^{\mathrm{BKNHC}} = H + \frac{K_1}{m_\zeta} + \frac{K_2}{m_\xi} + \frac{p_\eta^2}{2m_\eta} + \frac{p_\chi^2}{2m_\chi}, \tag{D2}$$

we have

$$\kappa_{\mathrm{BKNHC}} = \frac{1}{k_B T}\frac{dH_{\mathrm{T}}^{\mathrm{BK}}}{dt}, \tag{D3}$$

so that the invariant measure in phase space reads

$$d\mu = dx \exp\left[-\int_t dt \kappa_{\mathrm{BKNHC}}\right], \tag{D4a}$$

$$= dx \exp[-\beta H_{\mathrm{T}}^{\mathrm{BKNHC}}], \tag{D4b}$$

$$= dx \exp[-\beta H^{\mathrm{BKNHC}}]\exp[\zeta + \xi + \eta + \chi]. \tag{D4c}$$

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