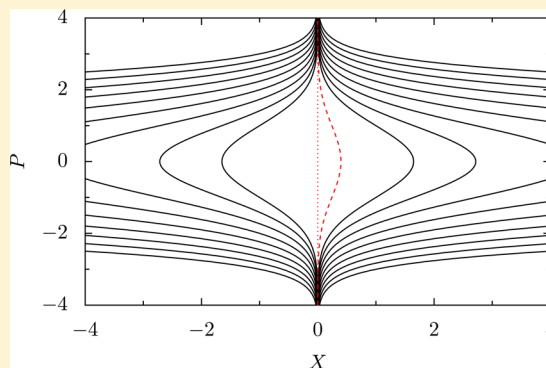


Thermostated Hamiltonian Dynamics with Log Oscillators

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ABSTRACT: With this work, we present two new methods for the generation of thermostatted, manifestly Hamiltonian dynamics and provide corresponding illustrations. The basis for this new class of thermostats is the peculiar thermodynamics as exhibited by logarithmic oscillators. These two schemes are best suited when applied to systems with a small number of degrees of freedom.



■ INTRODUCTION

Back in 1984, Nosé put forward a method for the generation of equations of motion that sample the canonical ensemble.¹ The method is based on the Nosé Hamiltonian, reading

$$H = \sum_i \frac{p_i^2}{2m_i X^2} + V(\mathbf{x}) + \frac{P^2}{2M} + k_B T \ln X \quad (1)$$

where a log oscillator with Hamiltonian $P^2/2M + k_B T \ln X$ is nonlinearly coupled to a “virtual” system (\mathbf{x}, \mathbf{p}) . The thermostatted dynamics of the “real” system are obtained after a time-rescaling and the application of a noncanonical transformation. The method was later further developed by Hoover² and is currently widely used and known as the Nosé–Hoover thermostat.

In this paper, we unveil those special thermodynamic properties of log oscillators that provide them with the power to act as thermostats and, based on them, show two more ways in which log oscillators can be employed to generate thermostatted dynamics. At variance with the method of Nosé, these methods are genuinely Hamiltonian, in the sense that the thermostatted dynamics are obtained directly from Hamilton’s equations of motion, with no need to perform a time rescaling nor use noncanonical transformations.^{3,4} Consequently, these methods not only constitute a numerical means but, as well, can even be implemented in situ with real experiments aimed at thermostating a physical system. The first of the two methods has been reported recently with a Letter; see ref 5. Its feasibility has been further discussed with a short account in ref 6, providing there the response that dispels a criticism raised by Hoover and co-workers.⁷

It is important to stress that, just like the Nosé–Hoover method, these methods only work provided the overall dynamics are ergodic, which might present a problem, especially when applied to small systems. In the case of

Nosé–Hoover thermostating, one possible solution was offered by Martyna et al.,⁸ who proposed the use of chains of Nosé–Hoover thermostats. Our first method, at least in the implementation that we have explored (that is, considering a system of particles that interact with each other and with a log oscillator via short-range, hard-core repulsion; see eq 21) seemingly is immune in reference to this ergodicity issue.^{5,9,10} Regarding our second method (see eq 29), the absence of ergodicity may present an issue; this second method, however, is sufficiently flexible as to overcome this challenge.

■ HELMHOLTZ THEOREM

The fact that logarithmic oscillators have a thermostating power is a consequence of their peculiar thermodynamic properties. In this section, we shall clarify in what sense it is meaningful to talk about the thermodynamics of mechanical systems that have only one or few degrees of freedom, as is the case of logarithmic oscillators, and demonstrate how to calculate their thermodynamic properties.

Our starting point is the salient equation of thermodynamics

$$\frac{\delta Q}{T} = \text{exact differential} = dS \quad (2)$$

also known as the heat theorem.¹¹ As early as 1884, Helmholtz proved that this mathematical structure of thermodynamics is inherent to the classical Hamiltonian dynamics of systems having only one single trajectory for each energy, which he called monocyclic systems.¹² Arguably, this seldom appreciated and rarely known fact was one of the cornerstones on which

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ergodic theory (which generalizes Helmholtz monocidicity) and statistical mechanics were later built up by Boltzmann and others.^{11,13–15}

The Helmholtz theorem goes as follows: Consider a classical particle in a confining potential $\varphi(X;\lambda)$, where λ is an external parameter. To each couple (E,λ) of values of the energy and the external parameter is associated one closed trajectory in the system phase space. For each trajectory, one can calculate the average quantities

$$k_B T(E, \lambda) := \left\langle \frac{P^2}{M} \right\rangle_{E,\lambda} \quad (3)$$

$$F(E, \lambda) := - \left\langle \frac{\partial \varphi}{\partial \lambda} \right\rangle_{E,\lambda} \quad (4)$$

where P and M are the particle momentum and mass, respectively, and $\langle \cdot \rangle_{E,\lambda}$ denotes the time average over the trajectory specified by (E,λ) . Noticing that $F(E,\lambda)$ is the average force that the particle exerts against the external agent, keeping the parameter λ at a fixed value, one realizes that

$$\delta Q = dE + F(E, \lambda)d\lambda \quad (5)$$

represents the heat differential. The Helmholtz theorem states that $1/T(E,\lambda)$ is an integrating factor for δQ

$$\frac{dE + F(E, \lambda)d\lambda}{T(E, \lambda)} = \text{exact differential} = dS \quad (6)$$

and that

$$S(E, \lambda) = k_B \ln \Phi(E, \lambda) \quad (7)$$

where

$$\begin{aligned} \Phi(E, \lambda) &= \left[2 \int_{X_-(E,\lambda)}^{X_+(E,\lambda)} \sqrt{2M(E - \varphi(X; \lambda))} dX \right] \\ &= \int dX dP \theta[E - H(X, P)] \end{aligned} \quad (8)$$

Here, $X_{\pm}(E,\lambda)$ are the turning points of the trajectory and $\theta(x)$ denotes the Heaviside step function. Accordingly, it is meaningful to call $T(E,\lambda)$ the temperature of the particle and $S(E,\lambda)$ its entropy. $S(E,\lambda)$ in eq 7 is also known as the Hertz entropy,¹⁵ or the Gibbs entropy.¹⁶

Once the function $S(E,\lambda)$ is known, one can then quickly calculate $T(E,\lambda)$ and $F(E,\lambda)$ in accordance with eq 6 as

$$T = \left(\frac{\partial S}{\partial E} \right)^{-1} \quad (9)$$

$$F = \frac{\partial S}{\partial \lambda} \left(\frac{\partial S}{\partial E} \right)^{-1} \quad (10)$$

and so obtain the thermodynamics of the system, such as the equation of state, specific heat, and so forth.

Following this scheme, in the next section, we will proceed to derive the thermodynamics of log oscillators and highlight the peculiar properties that provide them with thermostating power.

■ PECULIAR THERMODYNAMICS OF A LOG OSCILLATOR

Heat Capacity Is Infinite. Let us consider a log oscillator with the Hamiltonian

$$H_{\log}(X, P) = \frac{P^2}{2M} + k_B T \ln \frac{|X|}{b} \quad (11)$$

where M is the mass and b is some positive constant with the dimension of length. Figure 1 depicts some trajectories in phase

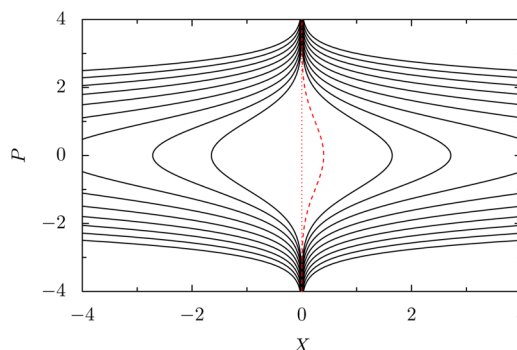


Figure 1. Black solid lines: Phase space trajectories of a log oscillator at energies of $E = 1/2, 1, 3/2, \dots, 9/2$; inner curves have lower energies. Red dashed line: The momentum distribution function, eq 17. Here $M = 1$ and $k_B T = 1$.

space of different energies. Solving the equation $H_{\log}(X,P) = E$ for X , one sees that the trajectories are given by the equations

$$X = \pm b e^{E/k_B T} e^{-P^2/2Mk_B T} \quad (12)$$

that is, the trajectories possess a Gaussian shape. Note that, accordingly, the maximal excursion grows exponentially with $E/k_B T$; $X_{\max} = b e^{E/k_B T}$. A straightforward calculation gives

$$\begin{aligned} \Phi_{\log}(E) &= \int dX dP \theta[E - H_{\log}(X, P)] \\ &= 2b \sqrt{2\pi M k_B T} e^{E/k_B T} \end{aligned} \quad (13)$$

Accordingly, the entropy, eq 7, reads

$$S(E) = \frac{E}{T} + k_B \ln[2b \sqrt{2\pi M k_B T}] \quad (14)$$

Using the Helmholtz theorem, we get

$$\left\langle \frac{P^2}{M} \right\rangle_E = \left(\frac{\partial S}{\partial E} \right)^{-1} = k_B T \quad (15)$$

This expresses the major feature of the thermodynamics of a log oscillator; all of its trajectories inherit one and the same absolute temperature, which is given by T , where T is the strength of the logarithmic potential. This fact is very peculiar. Consider, for example, the 1D harmonic oscillator, in this case, $k_B T(E) = E$, namely, the higher the energy, the higher the temperature. Similarly, this is the case for a particle in a 1D box, where $k_B T(E) = E/2$.

It therefore follows that the log oscillator possesses a spectacular property; it has an infinite heat capacity, that is

$$C(E) = \left(\frac{\partial T}{\partial E} \right)^{-1} = \infty \quad (16)$$

Thus, it mimics a bath composed of an infinite collection of harmonic oscillators¹⁷ or one with an infinite number of particles in a box.

Log Oscillators Sampling the Maxwell Distribution. Yet another peculiar feature of the log oscillator is that the

probability density $f(P)$ to find it with momentum P is given by the Maxwell distribution at temperature T

$$f(P) = (2\pi M k_B T)^{-1/2} e^{-P^2/2Mk_B T} \quad (17)$$

This holds independent of its energy E . To see this, consider the trajectory of the log oscillator of some energy E . The probability to find the system at X, P is given by the microcanonical distribution

$$\rho(X, P) = \frac{\delta[E - H_{\log}(X, P)]}{\Omega_{\log}(E)} \quad (18)$$

where $\delta(x)$ denotes Dirac's delta function, and

$$\begin{aligned} \Omega_{\log}(E) &= \int dX dP \delta[E - H_{\log}(X, P)] = \frac{\partial \Phi_{\log}(E)}{\partial E} \\ &= 2b \sqrt{2\pi M/k_B T} e^{E/k_B T} \end{aligned} \quad (19)$$

Therefore, the probability to find the log oscillator at momentum P is obtained by the marginal distribution

$$\begin{aligned} f(P) &= \int dX \rho(X, P) = \int \frac{dX \delta[E - H_{\log}(X, P)]}{\Omega_{\log}(E)} \\ &= \frac{1}{\Omega_{\log}(E)} \frac{\partial}{\partial E} \int dX \theta \left[E - P^2/2M - k_B T \ln \frac{|X|}{b} \right] \\ &= \frac{2}{\Omega_{\log}(E)} \frac{\partial}{\partial E} \int_0^{b \exp[(E - P^2/2M)/k_B T]} dX \\ &= \frac{2}{\Omega_{\log}(E)} \frac{\partial}{\partial E} b e^{[(E - P^2/2M)/k_B T]} = \frac{e^{-P^2/2Mk_B T}}{\sqrt{2\pi M k_B T}} \end{aligned} \quad (20)$$

where we have used $\delta(y) = d\theta(y)/dy$.

From eq 17, it is immediate to obtain $T(E) = \langle P^2 \rangle_E / M k_B = T$, in accordance with eq 15.

The red dashed curve in Figure 1 illustrates eq 17. When projecting the microcanonical distribution of the log oscillator onto the P axis, the Maxwell distribution is obtained, regardless of the energy.

METHOD I

The central feature of a thermal bath is that its heat capacity is infinite; hence, in this sense, a single log oscillator does indeed act like a thermal bath. On the basis of this observation, it is reasonable to expect that when a system interacts weakly with a log oscillator, the latter should induce thermostatted dynamics at temperature T in the system.

That this is indeed the case can be seen formally in the following manner.⁵ Consider the total Hamiltonian

$$H(\mathbf{x}, \mathbf{p}, X, P) = H_S(\mathbf{x}, \mathbf{p}) + H_{\log}(X, P) + h(\mathbf{x}, X) \quad (21)$$

where

$$H_S(\mathbf{x}, \mathbf{p}) = \mathbf{p}^2/2m + U(\mathbf{x}) \quad (22)$$

is the system Hamiltonian, and $h(\mathbf{x}, X)$ is a weak interaction term that couples the system to the log oscillator. Under the assumption that the total dynamics are ergodic, the probability density function $p(\mathbf{x}, \mathbf{p})$ for finding the system at (\mathbf{x}, \mathbf{p}) reads¹⁸

$$p(\mathbf{x}, \mathbf{p}) = \frac{\Omega_{\log}[E_{\text{tot}} - H_S(\mathbf{x}, \mathbf{p})]}{\Omega(E_{\text{tot}})} \quad (23)$$

where E_{tot} is the total energy of the compound system and

$$\Omega(E_{\text{tot}}) = \int dX dP d\mathbf{x} d\mathbf{p} \delta[E_{\text{tot}} - H(\mathbf{x}, \mathbf{p}, X, P)] \quad (24)$$

is the density of states of the compound system. Note that the shape of the distribution $p(\mathbf{x}, \mathbf{p})$ is given by the numerator, whereas the denominator only represents a normalization factor. Thus, from the fact that the density of states of a log oscillator is exponential in $E/k_B T$ (see eq 19), it immediately follows that

$$p(\mathbf{x}, \mathbf{p}) = \frac{e^{-H_S(\mathbf{x}, \mathbf{p})/k_B T}}{Z(T)} \quad (25)$$

where $Z(T) = \int d\mathbf{x} d\mathbf{p} e^{-H_S(\mathbf{x}, \mathbf{p})/k_B T}$. Thus, the constant temperature equations of motion read

$$\begin{cases} \dot{\mathbf{x}} = \mathbf{p}/m \\ \dot{\mathbf{p}} = -\partial_{\mathbf{x}} U(\mathbf{x}) - \partial_{\mathbf{x}} h(\mathbf{x}, X) \\ \dot{X} = P/M \\ \dot{P} = -k_B T/X - \partial_X h(\mathbf{x}, X) \end{cases}$$

where $\partial_{\mathbf{x}}$ denotes the gradient operator in the \mathbf{x} space and ∂_X is a short notation for $\partial/\partial X$. Note that for $h(\mathbf{x}, X) = 0$, that is, in the absence of interaction, the system undergoes constant energy dynamics.

Illustration. Reference 5 illustrates the numerical implementation of this method for small systems composed of few particles contained in a box and interacting through a repulsive hard-core potential

$$V_{\text{LJ}}(q) = \begin{cases} 0 & |q| > 2^{1/6} \sigma \\ 4\epsilon \left[\left(\frac{\sigma}{q} \right)^{12} - \left(\frac{\sigma}{q} \right)^6 \right] + \epsilon & |q| < 2^{1/6} \sigma \end{cases} \quad (26)$$

The main limitation of this method comes from the fact that, in practical realizations, the logarithmic potential needs to be truncated at low values of X , for example, by substituting it with

$$\varphi_b(X) = \frac{k_B T}{2} \ln \frac{X^2 + b^2}{b^2} \quad (27)$$

This truncation results in a deviation of the single-particle velocity distribution from the target Maxwell distribution. This deviation becomes more and more pronounced as the number of particles in the system increases (see Figure 3 of ref 5) and can be compensated for by rising the system energy as $E \approx f k_B T/2$, where f is the number of degrees of freedom of the system. This energy rising, however, is accompanied by an exponential increase of the corresponding length and time scales involved in the dynamics, which go as $e^{E/k_B T} \approx e^{f/2}$, thus limiting the applicability of the method to systems with a small number of degrees of freedom.

A prominent novel aspect of this method when compared to the other existing methods discussed in the literature is that it can be implemented not only with computer simulations but also in analogue simulations, provided that one is able to implement the Hamiltonian in eq 21 in a real experiment.⁵ Reference 6 discusses such an experimental feasibility of this method using cold atoms and laser fields.

Figure 2 illustrates this method for a system composed of either one particle or two particles in a one-dimensional box

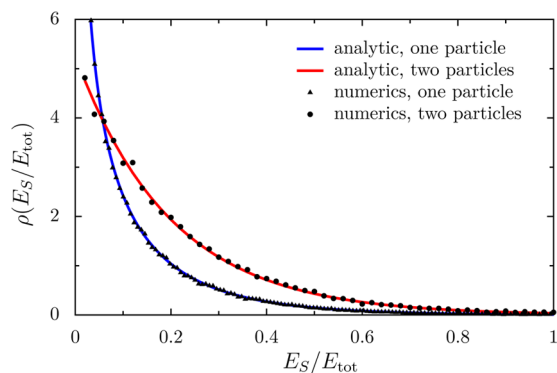


Figure 2. Illustration of Method I. Normalized probability density function of energy for a system of n particles in a 1D box performing short-ranged collisions (eq 26) with a truncated log oscillator (eq 27) of strength $k_B T = 15\epsilon$. The total simulation energy is $E_{\text{tot}} = 5k_B T$, the box length is $L = 10e^{E_{\text{tot}}/k_B T} \sigma \simeq 1484\sigma$, and the log oscillator cutoff length was set to $b = \sigma$. Black triangles: Numerical simulation with $n = 1$. Black dots: Numerical simulation with $n = 2$. Blue line: Gibbs distribution at temperature $k_B T = 15\epsilon$ for $n = 1$, as it follows from eq 28. Red line: Corresponding Gibbs distribution at temperature $k_B T = 15\epsilon$ for $n = 2$, as it follows from eq 28. This figure has been provided by Fei Zhan and is adapted here from our ref 10.

performing short-range, hard-core collisions (eq 26) with the truncated log oscillator in eq 27. It reports the probability $\rho(E_S)$ of finding the particle at energy E_S during a long simulation run. A symplectic integrator was used to produce the trajectory of the total system, and the initial condition was sampled randomly from the shell $E_{\text{tot}} = 5k_B T$. The numerically computed probability (relative frequency) $\rho(E_S)$ is compared to the expected Gibbs distribution calculated from eq 25 according to the standard rules of probability theory as

$$\rho(E_S) = \frac{e^{-E_S/T} \Omega_S(E_S)}{Z(T)} = \frac{e^{-E_S/T} \Omega_S(E_S)}{\int_0^\infty e^{-E_S/T} \Omega_S(E_S) dE_S} \quad (28)$$

where $\Omega_S(E_S)$ is the density of states of the system. In calculating it, we neglect the contribution coming from the short-range interaction, thus obtaining $\Omega_S(E_S) \propto E_S^{n/2-1}$, with $n = 1, 2$ being the number of particles in the system. For $n = 1$, this yields $\Omega_S(E_S) \propto E_S^{-1/2}$, while for $n = 2$, we find that $\Omega_S(E_S)$ is a constant. The agreement between theory and simulations is excellent. Further details and discussion can be found in refs 5 and 10.

METHOD II

An alternative method to produce thermostatted dynamics is to couple the system to a free particle via a logarithmic interaction potential. More explicitly, the statement is that the extended Hamiltonian

$$H(\mathbf{x}, \mathbf{p}, X, P) = H_S(\mathbf{x}, \mathbf{p}) + P^2/2M + k_B T \ln(\lg(\mathbf{x}, \mathbf{p}) - Xl/b) \quad (29)$$

produces thermostatted system dynamics, provided the (otherwise arbitrary) function $g(\mathbf{x}, \mathbf{p})$ induces ergodic dynamics of the total system.

To demonstrate this, consider the probability $\rho(\mathbf{x}, \mathbf{p}, X, P)$ to find the total system at $(\mathbf{x}, \mathbf{p}, X, P)$. Thanks to the ergodic assumption, this is given by the microcanonical distribution

$$\rho(\mathbf{x}, \mathbf{p}, X, P) = \frac{\delta[E_{\text{tot}} - H(\mathbf{x}, \mathbf{p}, X, P)]}{\Omega(E_{\text{tot}})} \quad (30)$$

hence

$$p(\mathbf{x}, \mathbf{p}) = \Omega(E_{\text{tot}})^{-1} \int dX dP \delta[E_{\text{tot}} - H_S - P^2/2M - T \ln(\lg(\mathbf{x}, \mathbf{p}) - Xl/b)] \quad (31)$$

Making the change of variable $X' = X - g(\mathbf{x}, \mathbf{p})$, one obtains, irrespective of $g(\mathbf{x}, \mathbf{p})$

$$p(\mathbf{x}, \mathbf{p}) = \frac{\int dX' dP \delta[E_{\text{tot}} - H_S - P^2/2M - k_B T \ln(lX'/b)]}{\Omega(E_{\text{tot}})} \quad (32)$$

Note that the numerator is the log oscillator density of states Ω_{log} taken at $E_{\text{tot}} - H_S$. Therefore, just as with Method I

$$p(\mathbf{x}, \mathbf{p}) = \frac{\Omega_{\text{log}}[E_{\text{tot}} - H_S(\mathbf{x}, \mathbf{p})]}{\Omega(E_{\text{tot}})} = \frac{e^{-H_S(\mathbf{x}, \mathbf{p})/k_B T}}{Z(T)} \quad (33)$$

The constant temperature equations of motion of this second method read

$$\begin{cases} \dot{\mathbf{x}} = \mathbf{p}/m + k_B T [g(\mathbf{x}, \mathbf{p}) - X]^{-1} \partial_{\mathbf{p}} g(\mathbf{x}, \mathbf{p}) \\ \dot{\mathbf{p}} = -\partial_{\mathbf{x}} U(\mathbf{x}, \mathbf{p}) - k_B T [g(\mathbf{x}, \mathbf{p}) - X]^{-1} \partial_{\mathbf{g}} g(\mathbf{x}, \mathbf{p}) \\ \dot{X} = P/M \\ \dot{P} = k_B T [g(\mathbf{x}, \mathbf{p}) - X]^{-1} \end{cases}$$

Note that for $T = 0$, the system undergoes constant energy dynamics.

It is important to repeat that thermostatted system dynamics are only reached if the global dynamics are ergodic. As illustrated below, this requirement is however not too restrictive because we have the freedom to choose the function $g(\mathbf{x}, \mathbf{p})$.

Illustration. To illustrate the method, we considered a quartic oscillator

$$H_S = \frac{p^2}{2m} + \frac{kx^4}{4} \quad (34)$$

We simulated the compound system dynamics using a symplectic integrator with a time step of $\Delta t = 10^{-2} b(M/k_B T)^{1/2}$ for a total simulation time of $\mathcal{T} = 1.287 \times 10^9 \Delta t$. In our simulations, we set $k_B T$, b , and M as units of energy, length, and mass, respectively. We took $(x_0, X_0, p_0, P_0) = (2, -1, 1, -1)$ as the initial condition, $k = k_B T b^{-4}$, and $m = M$. We computed the probability distribution function $\rho(E_S)$ to find the system at energy E_S and compared it with the target Gibbs distribution, eq 28. The latter reads

$$\rho(E_S) = \frac{e^{-E_S/k_B T} E_S^{-1/4}}{\int_0^\infty dE_S e^{-E_S/k_B T} E_S^{-1/4}} \quad (35)$$

where the factor $E_S^{-1/4}$ stems from the density of states of the quartic oscillator, $\int dx dp \delta[E_S - p^2/2m + kx^4/4] \propto E_S^{-1/4}$. We further computed the probability distribution function to find the system with a velocity of modulus v and compared it to the target Maxwell distribution, reading

$$p(v) = \frac{e^{-mv^2/2k_B T}}{\int_0^\infty e^{-mv^2/2k_B T} dv} \quad (36)$$

Following ref 5, the numerical evaluation of $\rho(E_S)$ proceeded by recording the value of E_S , once every 100 time steps. We divided the energy interval $[0, E_{\text{tot}}]$ into 50 bins and counted how many times E_S was within each bin, so as to construct a histogram, which, after normalization, gives an approximation to the actual $\rho(E_S)$. A similar procedure was followed for the calculation of $p(v)$.

To begin with, we chose $g(x, p) = x$. Notwithstanding the long integration time, the method fails to converge to the desired target distributions; see Figure 3a. This means that with the choice of $g(x, p) = x$, the overall dynamics is not sufficiently ergodic to make the system sample the canonical ensemble.

The ergodicity of the overall dynamics can be improved by choosing a different form for the function $g(x, p)$. Panel (b) of Figure 3 reports the result of a dynamical simulation of the same system as that in panel (a), with the same time step Δt and simulation time but with $g(x, p) = kx^4/4$, namely, we chose $g(x, p)$ as the system potential energy. While we found very good agreement between the computed energy probability distribution function and the Gibbs distribution, the agreement between the computed absolute velocity distribution and the target Maxwell distribution is still not very good. With $g(x, p) = \sin(kx^4/4)$ (see in panel (c) of Figure 3), reasonably good agreement between simulation and Maxwell distributions was achieved, while the agreement between the energy distribution and the Gibbs distribution was excellent. Excellent agreement was achieved with longer simulation times; see in panel (d) of Figure 3.

REMARKS

As emphasized above, ergodicity of the global dynamics constitutes the crucial prerequisite for the presented methods to work properly. Ergodicity suffices, and no stronger condition, for example, the system being mixing,¹⁹ is necessary. All that is needed for the system to sample the Gibbs distribution is that the compound system samples the microcanonical distribution. It should also be mentioned that ergodicity is a sufficient but not necessary condition for the methods to work, namely, in some cases, the methods might work even if ergodicity does not hold.

In Method I, whether ergodicity holds depends on the specific choice of the interaction energy $h(\mathbf{x}, X)$, which must be chosen in any case weak. In ref 5, $h(\mathbf{x}, X)$ was chosen as a hard-core, short-range repulsive interparticle potential (eq 26), and that was sufficient for achieving thermostating. In Method II, the ergodicity property depends on the choice of $g(\mathbf{x}, \mathbf{p})$, which in turn fixes the interaction term $k_B T \ln g(\mathbf{x}, \mathbf{p}) - Xl$. It must be emphasized however that our analysis shows neither formally nor numerically that the total dynamics are indeed ergodic in the examples presented but only that, loosely speaking, the system appears “ergodic enough” for the methods to work.

Note that in method II, the interaction term $k_B T \ln g(\mathbf{x}, \mathbf{p}) - Xl$ gives rise to long-range forces. Therefore, at variance with the implementation of Method I in ref 5, where the system and the “bath” interacted sporadically through almost instantaneous collisions, in Method II, they constantly influence each other due to the long-range force.

We have shown how different choices of $g(\mathbf{x}, \mathbf{p})$ can result in different ergodic properties of Method II. An important subject

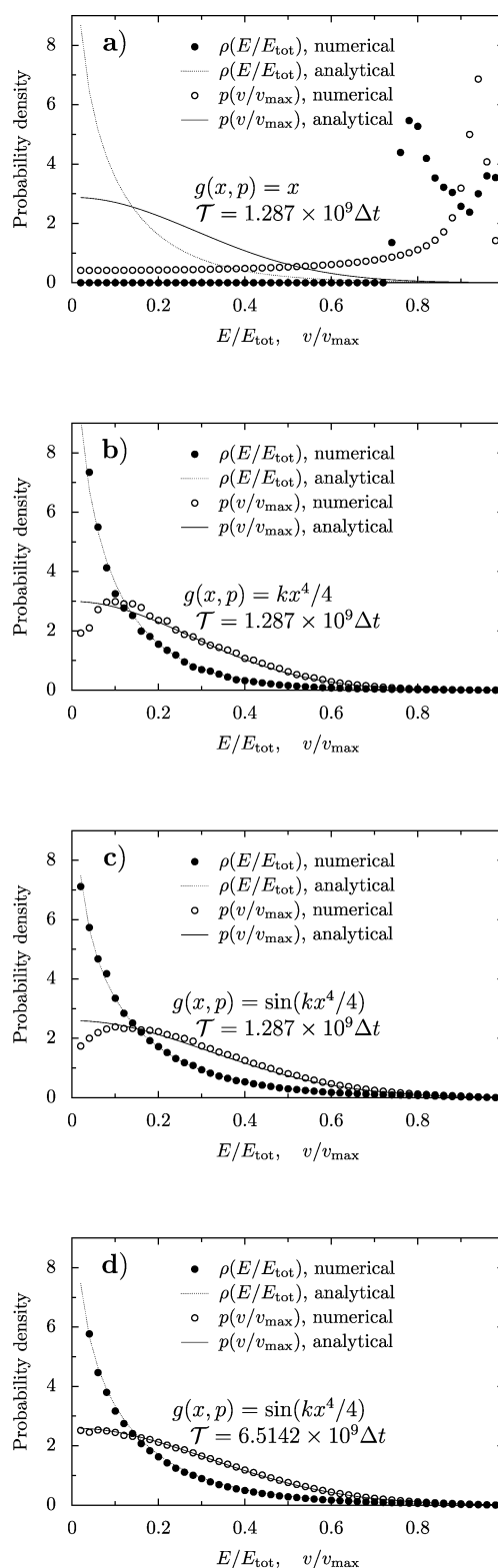


Figure 3. Illustration of Method II. Each panel reports the analytically and numerically computed probability distribution for the system energy E_S (rescaled by the total fixed energy E_{tot}) and system speed v , rescaled by the maximal speed $v_{\text{max}} = (2E_{\text{tot}}/m)^{1/2}$, for various choices of $g(x, p)$. Panel (d) has the same $g(x, p)$ as panel (c) but for a longer simulation time.

for further studies would be to derive a set of criteria for appropriately choosing $g(\mathbf{x}, \mathbf{p})$, given the properties of the system, as encoded in its Hamiltonian $H_S(\mathbf{x}, \mathbf{p})$.

Besides choosing $h(\mathbf{x}, X)$ or $g(\mathbf{x}, \mathbf{p})$, the ergodicity of both methods can be improved also by substituting the log oscillator with a multidimensional log oscillator, which will add more degrees of freedom to the whole system; see the Appendix.

In implementing Method II, we have replaced the logarithmic potential with the same truncated potential (eq 27) used for Method I. Therefore, just as with Method I, this truncation can lead to deviations to the target Maxwell distribution when the number of particles in the system increases. An interesting line for future studies would then be to put forward implementations that avoid the truncation and treat the singularity by some other means, which might allow for applying the methods to large systems as well.

CONCLUSIONS

With this study, we presented two Hamiltonian schemes that allow a system H_S to sample a canonical Gibbs distribution. This being so, the method of thermostating is achieved here in a deterministic time-reversal invariant and symplectic manner. Both schemes rest upon the spectacular thermodynamic property of logarithmic oscillators of having an infinite heat capacity. Hence, in our methods, a single log oscillator substitutes an infinite heat bath coupled weakly to the system. With our Method I, we couple the system weakly to a log oscillator where the absolute temperature T denotes the strength of the logarithmic potential. In Method II, we consider a composite system of H_S and a free particle that is coupled with a long-range log interaction of strength T to the system of interest H_S . Note that Gibbs thermalization occurs here independent of the interaction strength T , being either strong (large T) or weak (small T). A prominent property inherent to both schemes is that these are manifestly Hamiltonian.⁹ Also, at variance with the Nosé Hamiltonian (eq 1), our Hamiltonian functions possess standard (i.e., coordinate-independent) kinetic energy contributions. This fact in turn allows not only an implementation with numerical means but also a physical realization. This advantage should be contrasted nevertheless with the limitation that both methods inherit from performing a truncation of the logarithmic potential as in eq 27, which, as thoroughly emphasized in our previous accounts,^{5,6} limits an efficient thermostating to systems with a small number of degrees of freedom. Notably, the investigation of such nanoscale systems is in the limelight of present day research activities.^{20–23}

APPENDIX. F-DIMENSIONAL LOG OSCILLATORS

Consider an f -dimensional log oscillator

$$H_{\log}(\mathbf{X}, \mathbf{P}) = \frac{\mathbf{P}^2}{2M} + f k_B T \ln \frac{|\mathbf{X}|}{b} \quad (37)$$

where $\mathbf{X} = (X_1, X_2, \dots, X_f)$ and $\mathbf{P} = (P_1, P_2, \dots, P_f)$. For the phase volume $\Phi_{\log}(E) = \int_{H_S \leq E} d\mathbf{X} d\mathbf{P}$, one obtains

$$\Phi_{\log}(E) = \frac{(8\pi^2 b^2 M k_B T / f)^{f/2}}{\Gamma(f+1)} e^{E/k_B T} \quad (38)$$

where Γ denotes the Gamma function. Therefore, the density of states is exponential in $E/k_B T$, reading

$$\Omega_{\log}(E) = \frac{\partial \Phi_{\log}(E)}{\partial E} = \frac{(8\pi^2 b^2 M k_B T / f)^{f/2}}{k_B T \Gamma(f+1)} e^{E/k_B T} \quad (39)$$

Consequently, the methods presented above can also be implemented with an f -dimensional oscillator replacing the one-dimensional oscillator. In this case, Method I becomes

$$\begin{cases} \dot{\mathbf{x}} = \mathbf{p}/m \\ \dot{\mathbf{p}} = -\partial_{\mathbf{x}} U(\mathbf{x}) - \partial_{\mathbf{x}} h(\mathbf{x}, X) \\ \dot{\mathbf{X}} = \mathbf{P}/M \\ \dot{\mathbf{P}} = -[k_B T / \mathbf{X}^2] \mathbf{X} - \partial_{\mathbf{x}} h(\mathbf{x}, X) \end{cases}$$

and Method II becomes

$$\begin{cases} \dot{\mathbf{x}} = \mathbf{p}/m + [k_B T / (\mathbf{g} - \mathbf{X})^2] \sum_k (g_k - X_k) \partial_{\mathbf{p}} g_k \\ \dot{\mathbf{p}} = -\partial_{\mathbf{x}} U - [k_B T / (\mathbf{g} - \mathbf{X})^2] \sum_k (g_k - X_k) \partial_{\mathbf{x}} g_k \\ \dot{\mathbf{X}} = \mathbf{P}/M \\ \dot{\mathbf{P}} = [k_B T / (\mathbf{g} - \mathbf{X})^2] (\mathbf{g} - \mathbf{X}) \end{cases}$$

where \mathbf{g} , a short notation for $\mathbf{g}(\mathbf{x}, \mathbf{p}) = (g_1(\mathbf{x}, \mathbf{p}), \dots, g_f(\mathbf{x}, \mathbf{p}))$, is an f -dimensional field.

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Notes

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